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INDUSTRIAL MINERALS
and
ROCKS

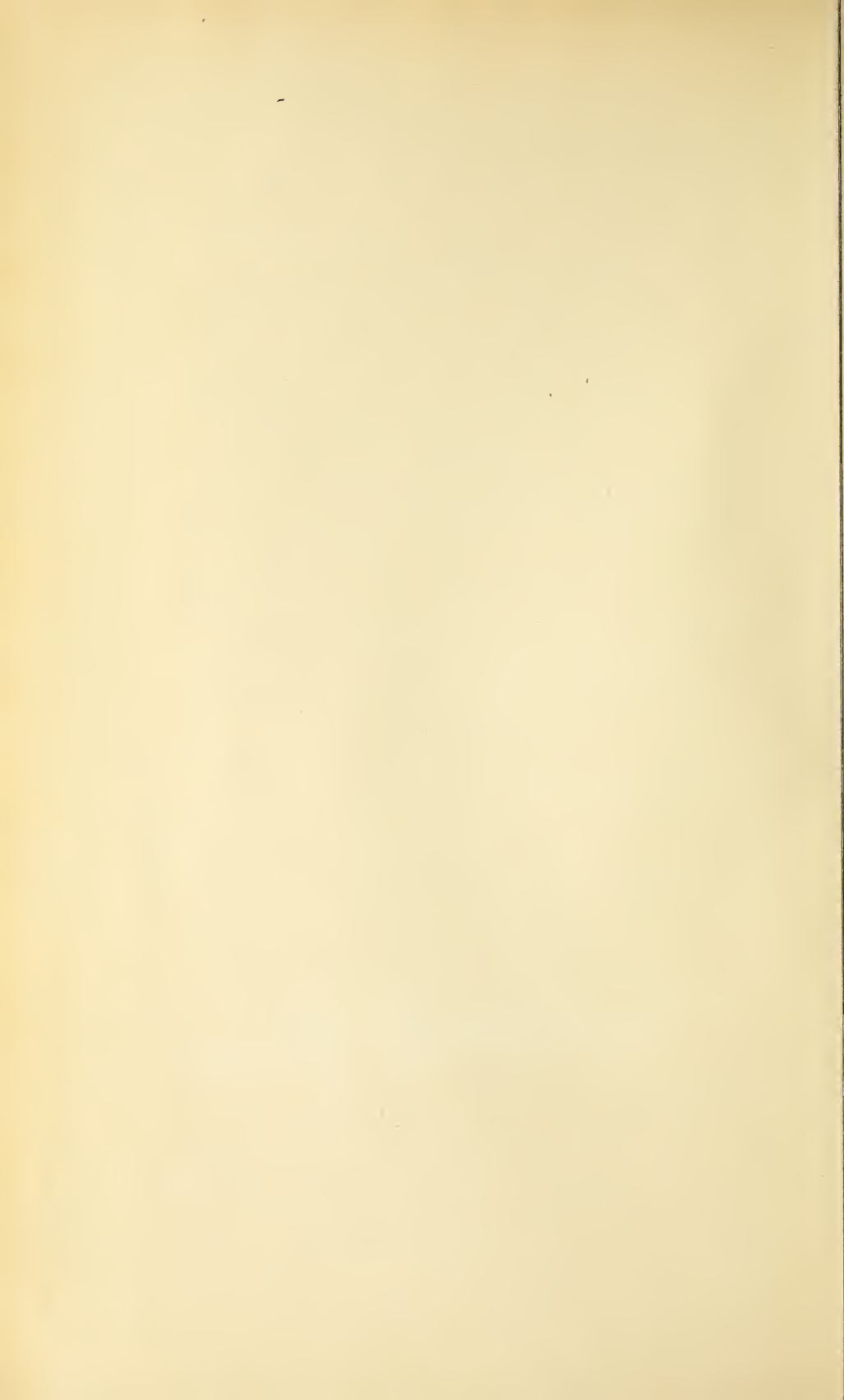


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AND ROCKS

The Seeley W. Mudd Series

INDUSTRIAL MINERALS AND ROCKS

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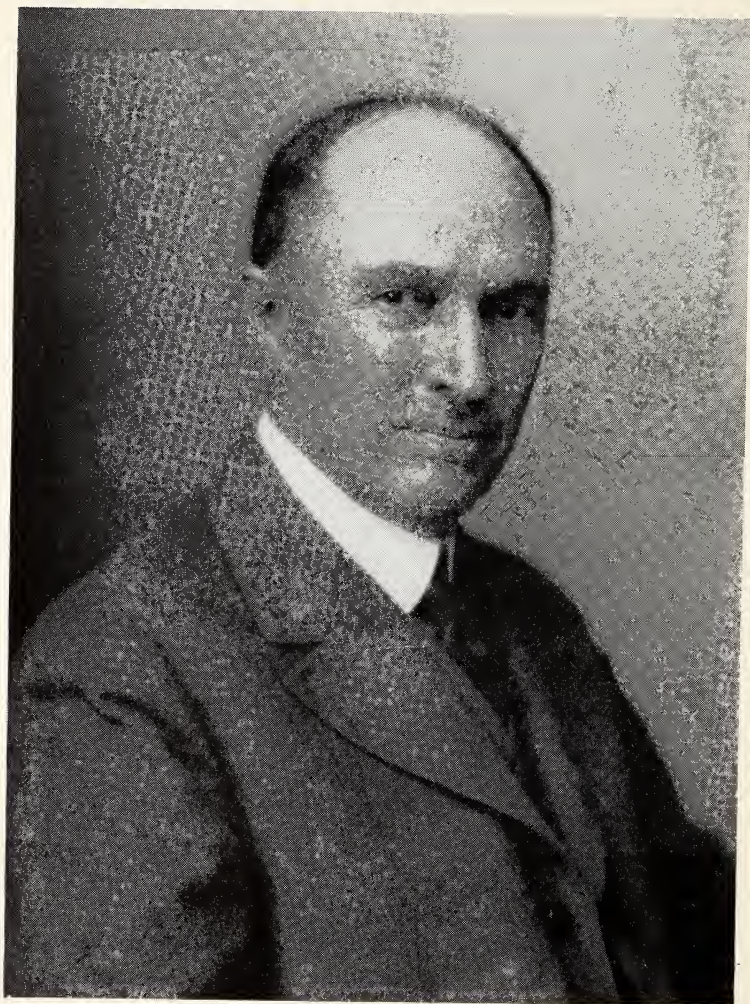
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INDUSTRIAL MINERALS AND ROCKS

(Nonmetallics other than Fuels)

SECOND EDITION
COMPLETELY REVISED

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Published by

THE AMERICAN INSTITUTE OF MINING
AND METALLURGICAL ENGINEERS

New York

1949

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THE MAPLE PRESS COMPANY, YORK, PA.

INTRODUCTION

THE FIRST edition of *Industrial Minerals and Rocks* was published in 1937. The growing demand, both in industry and for classroom use in colleges, led to a second printing a few years later. Now, after a lapse of ten years, it has been considered desirable to completely revise this work, to incorporate important technical developments in the intervening decade, and to bring statistical information up to date. This has resulted in the present edition II.

This work is composed of 51 chapters written by recognized specialists in the respective fields. Because of death, or for other reasons, several of the authors whose names appeared in the first edition have had to be replaced by others. In no other publication is there available so complete a collection of data on the so-called industrial minerals—a term which has now largely replaced “nonmetallic minerals” in technical usage.

As pointed out in the earlier edition, here is not only a large but a particularly fertile field for the engineer and technologist in the mineral industries. Only in recent years, and then only to a limited extent, have the search for, and the exploitation and beneficiation of, these minerals been conducted by men having professional engineering training. But more and more those who finance these operations are realizing the advantages of employing such men to manage and superintend their operations. The gradual exhaustion of surficial deposits and the consequent more elaborate mining methods; the need for mining ores of lower grade, resulting in the introduction of mechanical dressing and other types of processing; and the competition between materials, which demands that these things be done with the maximum efficiency—all these things require the highest possible skill, knowledge, and resourcefulness. The trend is distinctly toward the employment of technically educated men. The growing use of this work in technical schools is further evidence of the increasing demand for young engineers with specific training in this field.

Problems in the production of industrial minerals may differ in important respects from those found in metal or coal operations. Often such factors as color and other physical aspects are of high importance, whereas chemical analysis may or may not affect the utility of these materials.

Publication of this volume has been made possible by an appropriation made in 1946 by the Seeley W. Mudd Memorial Fund, administered by a committee composed of H. Foster Bain, Wilber Judson, and H. DeWitt Smith, with Louis S. Cates and A. B. Parsons ex-officio. In the Deed of Gift by which the fund was established, mention is made specifically of projects that would be of particular benefit to young engineers. The interest of Colonel Mudd in aiding younger men, particularly young engineers, has been taken into account by the Fund Committee, the Editorial Board, and the many authors and others who have contributed so freely of their time and knowledge in the preparation of this book.

To Oliver Bowles, Vice Chairman of the Editorial Board, is due much credit for organization and critical reading of manuscripts. The Institute is also indebted to other members of the Editorial Board and to the 49 individual contributors.

The U. S. Geological Survey, the U. S. Bureau of Mines, and the Canada Department of Mines and Resources have cooperated freely in this work in supplying statistical and other data. Many of the authors are specialists on the staffs of these organizations.

In view of the reception accorded the first edition, there can be little doubt of the usefulness of this work to those engaged in the production and use of industrial minerals and to those rising engineers and students who desire to take advantage of the growing field for engineers trained in these subjects.

NEW YORK, N. Y.
February 1, 1949

SAMUEL H. DOLBEAR.

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INDUSTRIAL MINERALS
AND ROCKS

INDUSTRIAL MINERALS AND ROCKS

(Nonmetallics Other than Fuels)

CHAPTER 1

ABRASIVES*

BY RAYMOND B. LADOO†

ABRASIVES include the substances, natural or artificial, that are used to grind, polish, abrade, scour, clean or otherwise remove solid material, usually by rubbing action but also by impact (sandblasting, for example). They do not include abrasive tools—for instance, lathe tools and files—or polishing agents such as waxes, which act by filling pores.

Detergents and cleaners whose action is chemical rather than physical are omitted although some chemical action polishes and cleaners may also contain solid abrasives; for example, many metal polishes.

GENERAL CONSIDERATIONS

The most important physical properties of materials that qualify them for use as abrasives are hardness, toughness (or brittleness), grain shape and size, character of fracture or cleavage, purity or uniformity. For making bonded grain abrasives such as grinding wheels, additional important factors are stability under high heat and bonding characteristics of grain surfaces. The economic factors of cost and availability are always important.

No one single property is paramount for any use. For some uses extreme hardness and toughness are needed, as in diamonds for drill bits; for others, the factors of greatest importance are hardness and ability to break down slowly under use, to develop fresh cutting edges when grains become worn—for example, in garnet for sandpaper, neither highly cleavable or friable grains nor extremely tough grains

* In this book separate chapters are devoted to Diamond, Diatomite, Tripoli, Pumice and Pumicite, Silica Sand and Quartz. In this chapter only brief reference will be made to these minerals. This chapter in the first edition of this book (1937) was written by V. L. Eardley-Wilmot, but has been almost entirely rewritten to bring it up to date.

† Consulting Engineer, Newton, Massachusetts.

are wanted. For still other uses, great hardness is objectionable; for example, abrasives for dentifrices and for glass-cleaning soaps. For the most efficient use in the more critical applications, the different types of abrasives are rarely completely interchangeable; thus, while crushed quartz and garnet are both used in sandpaper, the papers are not at all interchangeable in their use applications.

In the last analysis, the choice of a high-grade abrasive depends upon the quality and quantity of work done by the abrasive per unit of cost. Initial cost of an artificial abrasive may be much greater than that of a natural abrasive but the artificial abrasive may do so much better work than the natural one, and do it so much faster, that the ultimate cost will be less. It is on this basis that artificial abrasives have largely replaced natural abrasives for grinding metal.

CLASSIFICATION

Abrasives may be divided into two general classes, natural and manufactured. The former includes all rocks and minerals used for abrasive purposes without chemical or physical change other than crushing, shaping or bonding into suitable forms. Manufactured or artificial abrasives are made either by heat or chemical action from metals or mineral raw materials.

On page 3 is a list of the most important abrasives, classified as to inherent types and as to forms in which they are used industrially.

For most types of use there are manufactured products that can be substituted for the natural products, usually at higher initial cost but with higher efficiency. This is not always true; for example, there is no satisfactory manufactured substitute for garnet for making coated abrasive paper and cloth. For some abrasives whose use is gradually lessening—for instance, chaser stones—the making of manufactured substitutes has not been economically attractive, but for even such a low-priced commodity as sandblasting sand we have the substitutes of steel shot and silicon carbide grains.

The decline in the use of most natural abrasives and their replacement by manufactured abrasives has not been a net loss to the mineral industry, however, for virtually all manufactured abrasives are made from mineral raw materials.

HARDNESS AND ABRASIVE VALUE

Mineralogical hardness or "scratch" hardness as expressed in the Mohs scale is an important property in evaluating abrasive materials, but, as noted before, it is only one of several essential properties. The mineral hardness of pure crystal almandine garnet is about 7.5 but if the crystal is crossed by incipient fracture planes, or if it contains inclusions of pyrite, the apparent or useful hardness may be much lower.

Classification of Abrasives

Natural Abrasives

Superior Hardness (above 7 in Mohs' scale)

Diamond H—10

Corundum H— 9

Emery H—7 to 9

Garnet H—6.5 to 7.5

Intermediate Hardness (H—5.5 to 7)

Silica Abrasives

Buhrstone

Chalcedony

Chert

Flint

Quartz

Quartzite

Sandstone

Silica sand

Other Rocks and Minerals

Argillaceous limestone

Basalt

Feldspar

Granite

Mica schist

Pumice and pumicite

Quartz conglomerate

Inferior Hardness (H—under 5.5)

Apatite

Calcite

Chalk

Clay

Diatomite

Dolomite

Iron oxides

Limestone

Rottenstone

Siliceous shale

Silt

Talc

Tripoli

Whiting

Manufactured Abrasives

Boron carbide

Calcium carbonate (pptd.)

Calcium phosphate

Cerium oxide

Chromium oxide

Clay (hard burned)

Fused alumina

Glass

Iron oxides

Lampblack

Lime

Magnesia (pptd.)

Manganese dioxide

Periclase (artif.)

Silicon carbide

Tantalum carbide

Tin oxide

Titanium carbide

Tungsten carbide

Zirconium silicate

Metallic abrasives, including steel wool, steel shot, angular steel grit, brass wool, and copper wool

Porcelain blocks for mill liners and grinding pebbles

Types of Abrasive Products

Abrasive grains and powders, loose.

Abrasive grains bonded into wheels, blocks and special shapes.

Coated abrasives; grains bonded to paper and cloth.

Abrasive grains and powders; paste form; oil or water vehicles.

Abrasive grains and powders; brick and stick form; grease, glue and wax binders.

Natural rocks shaped into grindstones, pulpstones, chaser stones, mill stones, etc.

Natural rocks shaped into sharpening stones, such as oil stones, whetstones, scythe stones, razor hones, etc.

Natural stones shaped into rubbing and polishing stones, such as holystones and pumice scouring blocks.

Natural stones shaped into blocks for tube-mill and pebble-mill liners.

Pebbles, natural and manufactured, for grinding mills.

While the quartz grains in a sandstone have a hardness of 7, the bond holding the grains together may be so weak that the stone is valueless as a commercial abrasive. In artificially bonded wheels and stones, the hardness, strength and character of the bond is fully as important as the hardness of the abrasive grains. Thus, in an overall consideration of abrasive hardness of loose abrasive grains, both "scratch" hardness and toughness must be considered. In naturally or artificially bonded abrasive stones, bond characteristics is a third factor, which is most important.

The problem of abrasive hardness is further complicated by the inadequacies of our methods of testing hardness and of expressing relative values. The Mohs scale is inadequate both because the methods of testing are very crude and because the intervals between steps in the scale are not uniform; thus there is far less difference between hardnesses of 6 and 7 than between 9 and 10. Numerous attempts have been made to remedy these deficiencies. Ridgway, Ballard and Bailey⁴¹ proposed an extension of Mohs' scale to include artificially prepared substances. Knoop, Peters and Emerson³⁹ devised a diamond indentation method of measuring hardness, which gives reproducible results on a wide variety of materials and has the merit of giving definite numerical values over a wide range up to the hardness of the diamond.

Table 1 shows a comparison between these various hardness values for some of the harder materials.

TABLE 1—*Hardness of Mineral and Manufactured Products*

Mohs' Scale	Ridgway-Ballard-Bailey Extension to Mohs' Scale	Knoop-Peters-Emerson Diamond Indentation Values
Orthoclase, 6	Orthoclase or periclase, 6	Fused quartz, 475
Quartz, 7	Vitreous pure silica (fused quartz), 7	
Topaz, 8	Quartz; Stellite, 8	
	Topaz, 9	Fused alumina, 1635 Silicon carbide, 2000 Boron carbide (molded), 2230
	Garnet, 10	
	Fused zirconia; tantalum carbide, 11	
Sapphire, 9	Fused alumina; tungsten carbide, 12	
	Silicon carbide, 13	
	Boron carbide, 14	
Diamond, 10	Diamond, 15	

TYPES OF ABRASIVE PRODUCTS

A general classification of the types of abrasives products has been given on page 3. Specific information is given in more detail in the following pages, particularly for natural abrasives, under some of the separate mineral headings. However, many abrasive products are made from a variety of raw materials, both natural and arti-

ficial, and a general treatment of the more important products can be given. The uses and applications for abrasives cover such a large and diversified field that only an exhaustive treatise could hope to cover all or a substantial part of them. Only examples of some of the more important uses can be included here.

Abrasive Grains

Abrasive grains are produced from a wide variety of materials, both for use as grains and for incorporation into other products. Thus abrasive grains are not only important products of themselves but are the starting point for making bonded shapes, coated abrasives, abrasive tools, polishes, cleaners, and grinding pastes.

For sandblasting, in addition to silica sand, are used other natural mineral grains such as corundum, garnet, flint and chert as well as manufactured products such as fused alumina, silicon carbide, and steel shot. For this use the physical properties of hardness, toughness, grain shape, grain size, uniformity and specific gravity are important. For virtually all uses a hardness of 7 or more is needed. Grains should be tough, so that they will not disintegrate readily under impact. For some uses rounded grains are considered desirable, for others sharp cutting edges are favored. Uniformity of grain size and other physical properties is always desired. The higher the specific gravity, the greater the force of impact for grains of equal size. Each use has its own special requirements.

In general, any mineral or artificial product can be considered as a possibility for sandblasting if it can be produced as uniform graded grains that are at least as hard, tough, and dense as quartz sand.

Common uses for "sandblasting" are: cleaning stone and concrete, cleaning metal castings, preparing surfaces for painting, etching of glass and plastics.

Loose grains of relatively coarse sizes are used for sawing stone, grinding plate glass, surfacing stone. (Quartz sand, garnet, corundum, emery, aluminum oxide, silicon carbide.)

Grains of somewhat smaller sizes are used for grinding lenses, rough polishing of building stone and plate glass, rough polishing of gems and ornamental stones. (Quartz sand, garnet, corundum, emery, aluminum oxide, silicon carbide.)

Fine-grained powders are used for polishing and lapping of all kinds of glass, stone, metals, plastics, wood finishes. (Rouge, crocus, tin oxide, chromium oxide, cerium oxide, rottenstone, pumice, diatomite, tripoli, ground silica, clay, whiting.)

In one method for drilling small holes in glass, porcelain, gem stones, and similar materials, a brass tube is used, charged with diamond, corundum, emery, aluminum oxide, silicon carbide or boron

carbide dust, in a vehicle of water, oil, or grease. Diamond-tipped drills are also used for this purpose.

Ground feldspar, fuller's earth, and perhaps other materials, are used as nonskid dusting agents for oily floors.

Bonded Abrasives

Abrasive grains, closely sized, are bonded and pressed or molded into a wide variety of bonded abrasives such as grinding wheels. Originally the abrasives in such products were corundum or emery but with the introduction of the electric-furnace abrasives, aluminum oxide and silicon carbide, the use of the natural abrasives has very greatly declined, although they are still needed for special applications. There are five main types of bonded abrasives, depending on the type of bond and method of manufacture: (1) vitrified or ceramic shapes, with a clay-feldspar bond, which is vitrified in ceramic kilns; (2) silicate wheels, in which sodium silicate is the binder; (3) resinoid wheels with hard synthetic resin binders; (4) rubber or elastic wheels with a hard-rubber bond; and (5) shellac bond wheels. All types of wheels are, or may be, made with any one of these four abrasives, natural or artificial. Special wheels are made from diamond powder. At one time low-temperature bonded wheels made with garnet abrasive were used for some purposes.

The problem of proper bonding of boron carbide grains has not yet been solved.

The choice of the kind of abrasive and type of bond depends upon the use for which the wheel is intended. Ordinary all-purpose wheels usually are of the vitrified bond type.

Wheels are made that vary in at least five physical properties, aside from size and shape: (1) type of abrasive grain (aluminum oxide, silicon carbide, corundum, emery, diamond, etc.); (2) grain (size of abrasive grains, 8 to 600-mesh); (3) grade (strength of bond, 18 to 20 grades); (4) structure (grain spacing, 10 to 12 spacings); (5) bond (vitrified, etc., five bond types).

When all these variables are combined with an almost infinite number of sizes, shapes and spindle diameters that are standard or can be had on special order, the complexity of the abrasive-wheel business is apparent.

In addition to grinding wheels, bonded abrasives are made up into blocks, bricks and sticks for sharpening and polishing stones such as oil stones, scythe stones, razor and cylinder hones. Curved blocks and segments are made, which can be combined into large wheels such as pulp-stones or used mounted or unmounted for grinding or polishing the interior or exterior of curved surfaces.

Rectangular tile with abrasive-grain surfaces are made for nonslip floor and stair treads.

Rubber pencil and ink erasers contain abrasive grains and similar soft rubber wheels, sticks, and other forms, are made for finishing soft metals.

Coated Abrasives

Coated abrasives consist of sized abrasive grains cemented to paper or cloth backing. Originally "sandpaper" perhaps was coated with sand but today crushed quartz is used on silica-type papers because its grains have much sharper cutting edges. Crushed glass formerly was used to

TABLE 2—Size Grades for Abrasives

Modern Mesh Designation	Old Garnet Scale	Flint Scale	Emery Scale
400			
320			
280	8/0		
240	7/0 ^a	5/0	
220	6/0	4/0	
		3/0	
180	5/0		3/0
150	4/0	2/0	2/0
120	3/0		1/0
		1/0	
100	2/0		
		$\frac{1}{2}$	$\frac{1}{2}$
80	1/0		1
		1	
60	$\frac{1}{2}$		1 $\frac{1}{2}$
50	1	1 $\frac{1}{2}$	2
		2	2 $\frac{1}{2}$
40	1 $\frac{1}{2}$		
		2 $\frac{1}{2}$	
36	2		3
30	2 $\frac{1}{2}$	3	
24	3	3 $\frac{1}{2}$	
	3 $\frac{1}{2}$ ^b		

^a Approximately 220-mesh Tyler.

^b Approximately 20-mesh Tyler.

surface "glass" paper, but is now obsolete. The principal abrasives used today for this purpose are crushed quartz, garnet, aluminum oxide and silicon carbide. Most "emery" cloth today is coated with silicon carbide or aluminum oxide. "Flint" paper in the United States is coated with crushed quartz but true flint is used in Europe.

All abrasive grains, natural or artificial, are made by graded crushing and close sizing. Crushing usually is done wet in rolls to avoid making extreme fines (for which there is little demand) with close screening between sets of two rolls each. Products are washed in classifiers

to remove slimes, then are dried, passed through magnetic separators to remove iron-bearing minerals, and again very closely sized in screens. Such careful sizing is essential to prevent contamination of grades by coarser grains. The finest powders are sized by water flotation and sedimentation.

In earlier practice, grade numbers were more or less arbitrarily assigned to grain sizes and, unfortunately, the garnet, flint and emery scales were all different. Artificial abrasives were given numbers based on bolting-cloth mesh designations, which roughly correspond with but are not exact equivalents of standard testing sieve meshes. Gradually garnet and "flint" paper grade numbers have come to include both the old and the new numbers. Table 2, after Tyler,⁴⁵ shows the relationship between the different scale sizes.

The bond for coated abrasives may be either glue or a synthetic resin adhesive. The backing is either paper or cloth.

Garnet and "flint" papers and cloths are most widely used for wood, leather, hard rubber, plastics, felt, and rubbed paint and varnish finishes on metals. Abrasives coated with silicon carbide and aluminum oxide are used chiefly in the metal-working industries.

More detailed information on coated abrasives is contained in the section on garnet later in this chapter.

Grains and Powders for Soaps, Cleaners and Polishes

Many different materials, mostly natural but some manufactured, are used in making soaps, cleaners and polishes.

In hand and scouring soaps are found feldspar, pumice and pumice, sand, ground quartz, tripoli, diatomaceous earth, clay, and wood flour. Often cheapness is the primary factor in the selection of the abrasive, in spite of extravagant claims by some manufacturers. The commercial success of a cleanser depends largely upon advertising and sales ability rather than on superiority over competitive products, provided a fairly good product is made, but occasionally the abrasive is a really important factor. A household cleanser should not contain quartz or any mineral of equal or greater hardness, as glasses and enamels are nearly all 6 or lower in hardness and are scratched by any grain of equal or greater hardness. The abrasive should not contain calcium carbonate, calcium sulphate, or other easily reactive lime compounds because lime reacts with most soaps to form insoluble substances, which are very difficult to remove from glass or enamel surfaces.

An ideal mineral abrasive for this use might be a mineral or rock between 3 and 5 in hardness occurring in abundance in easily mined deposits, close to rail transportation and within a reasonable freight-haul distance of important markets. The material should be uniform in

texture and physical properties and contain no impurities harder than 6 and no easily reactive impurities such as lime compounds.

The ultimate grain size of abrasives in this group depends upon the properties desired in the finished product. It ranges from extremely fine air-separated and water-floated particles in the micron sizes, much finer than 325-mesh, up to 100-mesh or even coarser for heavy-duty scouring soaps.

INDUSTRIAL DIAMONDS

Diamonds are reviewed in detail in chapter 35, therefore only their uses as abrasives are outlined here.

By far the largest producer of industrial diamonds is the Belgian Congo and the Gold Coast, Sierra Leone, Angola and the Union of South Africa supply most of the remainder. Brazil, which once was an important producer, in 1945 accounted for only about 2 pct of the world's total production of diamonds. At the peak of its war use (1944), the United States imported 12,614,507 carats of industrial diamonds, valued at \$22,861,401.

There are three types of industrial diamonds: (1) bort, which includes off-color, flawed or broken fragments of diamonds unsuitable for gems, (2) carbonado, or black diamond, which is a very hard and extremely tough aggregate of very small diamond crystals, and (3) ballas, a very hard, tough, globular mass of diamond crystals radiating from a common center. Carbonadoes come only from Bahia, Brazil; ballas chiefly from Brazil but a few from South Africa. Bort comes from all diamond-producing centers.

The industrial diamond has become one of the most important and essential materials in modern industry. Diamond drilling, once used only for locating metallic ores, is now widely used for exploring non-metallic mineral deposits, for exploring geologic structures for foundations for dams, buildings and heavy machinery, for exploring internal condition in heavy concrete structures such as dams, for stope mining, explosive demolitions under special conditions, and other purposes.

Industrial diamonds were of greatest importance in all of our war activities, particularly in mechanical production operations of high speed, precision grinding and sawing.

Some of the most important uses are: diamond-drill bits for drilling rock and concrete; diamond dies for wire drawing; diamond-tipped tools for truing abrasive wheels and for turning and boring hard rubber, fiber, vulcanite, hard plastics, etc.; diamond-toothed saws and rim-impregnated saws for sawing stone, glass, quartz, metals, etc.; wheels, both for grinding and for cutoff work, in which the working face consists of diamond dust bonded with a resinoid, metal or ceramic product; diamond-tipped tools for cutting glass and for engraving gems; diamond powder for cutting gems. High-speed tool steels, cemented car-

bides and other exceedingly hard, tough alloys can be cut and shaped efficiently only with diamond tools, and diamond-tipped tools are essential for the rapid and accurate shaping, truing and dressing of abrasive wheels. Our World War II mechanical production could not have been achieved without industrial diamonds.

CORUNDUM AND EMERY

Corundum, a naturally crystallized oxide of aluminum, is next to the diamond, the hardest natural mineral known. While the transparent varieties, ruby and sapphire, may have been used by the ancients as abrasives for carving and shaping gems, the industrial use of grain corundum is perhaps only about a century old. However emery, which is a natural mixture of corundum, iron oxide, and other materials, has been used as a commercial abrasive for several centuries.

When the artificially prepared electric-furnace abrasives, silicon carbide and fused alumina, began to become commercially available at reasonable prices, they gradually replaced natural corundum and emery. These natural minerals declined in importance until now they are used only for limited small-scale applications under special conditions and for special products. Corundum still continues to be superior to artificial abrasives for use in snagging wheels used in finishing heavy iron and steel castings and forgings and for grinding optical lenses. War demands for these special uses made it necessary to stimulate in every possible way the production of corundum during both World Wars.

It seems likely that continued discoveries and improvements in making artificial abrasives will eventually—perhaps in the near future—make the use of these natural abrasives obsolete.

The story of corundum and emery, then, becomes chiefly historical and as such is largely outside the scope of this chapter. Detailed accounts of the history of this industry will be found in the books listed at the end of the chapter.

Composition

Corundum, theoretically, is pure crystallized alumina (Al_2O_3), with 52.9 pct aluminum and 47.1 pct oxygen. Emery is not a pure mineral but is a natural mixture of alumina with iron oxides, Fe_2O_3 or Fe_3O_4 , plus varying amounts of impurities. Analyses of typical corundum and emery are given in Table 3.

Mineralogically, emery is divided into three varieties: (1) true emery, (2) spinel emery, (3) feldspathic emery. It is regarded as a mechanical admixture.

True emery is a mixture of corundum and magnetite, with or without hematite derived from the magnetite, such as the Greek and Turkish emery, and is usually of a reddish black tint.

TABLE 3—*Analyses of Emery from Different Localities*

Locality	Alumina	Silica	Magnetic Iron Oxide	Lime	Magnesia	Water	Total
Greece:							
Naxos.....	62.64	4.90	31.41	0.45	0.06	1.04	100.50
Naxos.....	68.53	3.10	24.10	0.86		4.72	101.31
Naxos.....	57.69	6.36	30.87	0.89	0.20	3.99	100.00
Nicaria.....	75.12	6.88	13.06	0.72		3.10	98.88
Turkey:							
Kulah.....	63.50	1.61	33.25	0.92		1.90	101.18
Gumuch.....	60.10	1.80	33.20	0.48		5.62	101.20
Samos.....	70.10 ^a	4.00	22.21	0.62		2.10	99.03
U.S.A.:							
Virginia.....	45.38	2.53	41.23	0.06	5.71	1.32	96.23
Chester, Mass..	50.02	3.25	44.11			^c	97.36
New York.....	59.22 ^b	0.84	30.68		3.54	2.70	96.98
New York.....	50.10	14.32	28.17	0.84	4.31	^c	97.74

^a Also contains 3.72 pct TiO₂ (ilmenite) and some of the alumina as spinel.

^b Also contains 3.28 pct TiO₂ (ilmenite) and some of the alumina as spinel.

^c No data.

Spinel emery is a mixture of spinel (pleonastehercynite) corundum and magnetite, the corundum being present in variable proportions and sometimes entirely lacking. It is usually a heavy, black, fine-grained aggregate with dark gray crystals of corundum appearing in the best varieties. The crystals often are cracked and considerably altered to hydrous mica. This kind is mined in New York and Virginia in the United States.

Feldspathic emery is similar to the spinel but contains in addition from 30 to 50 pct plagioclase feldspar. Pure magnetite often is found in streaks within this mass.

There are at least three recognized grades of emery: Greek or Naxos, Turkish, and American, of varying chemical and physical properties.

Properties

Hardness—Corundum is the type mineral for No. 9 in the Mohs scale, but varies somewhat depending upon purity. Pure sapphire is the hardest variety. Emery varies from 7 to nearly 9.

Specific Gravity—Specific gravity of corundum is 3.93 to 4.10; of emery, 2.7 to 4.3.

Melting Point—The melting point of corundum is above 1950°C; of emery, variable depending on composition.

Color—Corundum is gray, blue, red, green, yellow, black, brown, white or colorless. Emery is dark gray to blue black, sometimes mottled; sometimes reddish black due to hematite inclusions.

Streak—Streak of corundum is white; of emery, brown to black.

Luster—Corundum is vitreous or adamantine; emery is dull, earthy.

Index of Refraction—Corundum is 1.760 to 1.768, low double refraction, strong pleochroism. It is transparent to opaque; also very permeable to X-rays, a property that serves to distinguish true corundum gems from artificial stones.

Crystallization and Cleavage

Corundum crystallizes in the rhombohedral division of the hexagonal system, in six-sided barrel-shaped crystals, tapering from the center to the ends, either short and stubby or long and fairly slender. A pronounced basal cleavage at right angles to the long axis gives smooth terminal planes, which usually show deep striations forming equilateral triangles. The prism faces usually show crosshatching due to lamellar twinning. In addition to the basal cleavage, there are usually incipient rhombohedral parting planes at nearly right angles. Fracture is conchoidal. Tenacity is brittle to tough.

Corundum occurs in three general phases: (1) as fairly large, distinct crystals, (2) in granular form as small crystals or irregular grains in schists and gneisses, and (3) in massive or block structure with parting planes poorly developed.

Emery occurs in compact massive aggregates, from fine to coarse in grain size with no crystal structure, cleavage or parting.

Origin and Mode of Occurrence

CORUNDUM

Corundum is known to occur in about 20 kinds of rocks and in about 35 different countries throughout the world. The mineral usually is associated with peridotite in the United States, nepheline syenites in Canada and feldspathic rocks in India and South Africa. The origin of corundum has been discussed in some detail by several authors, among whom are A. E. Barlow,¹ J. H. Pratt,¹² A. L. Hall, T. H. Holland and others, the latter summarized in the Canada Mines Branch report.² It appears generally accepted that corundum was one of the first constituents to crystallize out from the molten magma and, further, that in certain supersaturated magmas the whole of the excess of the alumina separates out as corundum, provided that the iron, magnesia and silica present are low; if these are high, it separates out as spinel, cordierite and other minerals (p. 24 of ref. 2). Corundum, consequently, does not occur in the immediate vicinity of free silica, such as quartz.

The South African corundum is invariably associated with pegmatite intrusions into basic rocks.⁴

EMERY

Emery usually occurs in crystalline limestones and schists, also in peridotite and diorite. It is often associated with chlorite in hornblende schists (for details, see references at end of chapter).

Geographical Distribution and Production

Corundum deposits of commercial interest have been found only in United States, Canada, Union of South Africa, India, Madagascar and Russia. Deposits have been reported in many other countries and a few have been developed to a small extent but are not at present considered of commercial importance.

Emery has been produced commercially on an important scale in United States, Greece, Turkey, and Russia. A deposit in Bavaria has produced a small tonnage and unimportant deposits have been reported in Australia, Uruguay, and Persia (Iran).

CORUNDUM—UNITED STATES

Corundum has been mined in the United States at Laurel Creek, Rabun County, Georgia; at Corundum Hill, Macon County, and at Webster, Jackson County, North Carolina; at Clover, York County, South Carolina; and in Gallatin County, Montana. A few other deposits in the southeastern belt have produced small tonnages and unworked occurrences have been reported in California, Colorado, and Idaho. In North Carolina and Georgia the corundum occurs in irregular elongated bodies, a few inches to 15 ft thick, in contact zones between peridotite and schists and gneisses.

Regular production started about 1880 at Laurel Creek, Georgia, and continued from there and other deposits in the area at a rate of 500 to 650 tons per year until 1905. From then until World War I in 1917, there was no domestic production. In 1917 and 1918 a total of 1185 tons was produced and then no further production until World War II in 1943. During the war domestic deposits were reexamined in detail by governmental agencies, particularly in North and South Carolina and Montana. A few small experimental shipments were made but successful operation could not be predicted and all activity was finally discontinued in spite of the fact that demand continued acute until the end of the war.

The conclusion is unescapable that, even under high war demand, a domestic corundum industry cannot be supported from present known deposits.

From the termination of domestic production in 1905 until 1921, most of the corundum used in the United States came from Canada. From 1921 to date most of our corundum has come from the Trans-

vaal, in the Union of South Africa, and small occasional imports from Rhodesia, Madagascar, and India.

Domestic consumption of corundum, as indicated by import statistics since 1924 (when separate import statistics were first reported), have ranged from a low of 188 tons during the depression year of 1932 to a high of nearly 6000 tons in 1941, and has averaged 2000 to 4000 tons. Imports statistics given are for corundum ore, but imports of finished grain, paper and cloth, and wheels have been very small, both in value and in volume.

CORUNDUM—WORLD SOURCES

South Africa

The chief world sources of corundum both prior to and during World War II were in southern Africa, particularly the Transvaal, but some production has come from Southern Rhodesia, Mozambique (Portuguese East Africa), Nyasaland, Namaqualand (Cape Province). Very small production is noted from Tanganyika.

During World War II, the Foreign Economic Administration of the United States stimulated, in every possible way, the search for and development of new deposits and the increase in production from operations previously exploited but, in spite of this stimulation, production did not increase greatly. From 1934 to 1940, exports (chiefly to U. S.) ranged from 1540 tons (1938) to 4853 tons (1936), yet in 1944 exports were only 3898 tons and in 1945 only 4762 tons. However, it is stated that if programs under way had not been abandoned at the close of the war, average monthly production of more than 600 tons could have been reached.

Metcalf⁸ has given the most complete recent picture of South African corundum, from which most of this section is quoted or abstracted (see also ref. 9), as follows:

"This material is mined from both "reef" and eluvial deposits largely in northern and northeastern Transvaal. The rocks in which corundum occurs as a primary constituent in northern Transvaal are scattered over an area of more than 3000 square miles, centering around Bandolierkop. They are lenses or veins intruded into basic rock masses.

"Of the primary occurrences, the plumasite deposits in northern Transvaal are the most widespread. The typical plumasite rock is composed of feldspar and dull-gray crystals of corundum. The marundite deposits are found in the eastern part of the Transvaal corundum area. The typical marundite is a coarsely crystalline rock in which the corundum is embedded in scaly or rosette-shaped aggregates of margarite.

"Corundum deposits of the gneissic type are less common, but they occur in several important areas. In this type, the corundum rock is composed of feldspar-biotite gneiss. As corundum is highly resistant

to weathering, it is found in detrital or eluvial deposits, usually in close proximity to the primary corundum-bearing rocks. In the past, a large part of the material produced was derived from the detrital deposits."

The 1945 production consisted roughly of 44 pct Crystal grade, 28 pct Boulder grade, and 28 pct Concentrates. Crystal grade comes from: (1) eluvial deposits from which loose corundum crystals in decomposed rock are won by hand picking or rough screening, and (2) reef deposits from which the corundum is obtained from partly decomposed reef rock, by hand cobbing and primitive crushing, screening and jigging devices. Boulder corundum is massive material, usually occurring in small deposits associated with plumasite ores. Concentrates, as the name implies, consists of concentrates made by more formal milling processes.

"Large-scale mining" in the Transvaal corundum fields has not been undertaken owing to a combination of local and rather special conditions. Deposits generally are quite small, unevenly distributed over a wide area, neither persistent nor regular in character, and not constant as to the amounts of corundum present. Only one type—crystal corundum—normally enjoys a reasonably steady, continuing market. Individual operations are small, varying from less than a ton to around 30 tons a month. The diggers, for the most part without capital, work only sporadically.

"The ore is mined from open pits, generally not deeper than 20 ft. Picks and shovels, both for alluvial and reef deposits, commonly are the only equipment used, with some hand drilling and blasting in the harder rock. Hand-operated or power-driven cranes are employed in some of the deeper mines that reach 100 ft or more in depth, although in many operations the mined rock is shoveled from one platform to another until the surface is reached. Except where boulder corundum is recovered and marketed as such, efforts are made to recover as high a percentage of "crystal" corundum as possible.

"In alluvial workings a coarse screening, either by hand or mechanically, is followed by fine screening, the latter over $\frac{1}{8}$ -in. mesh. The coarse screen product may be washed. Because of the high specific gravity of corundum, recovery by hand sieving is fairly efficient. The finer sizes through $\frac{1}{8}$ -in. openings are lost. Most of the corundum from the so-called reef or primary deposits has been obtained from rocks more or less weathered or softened, or from naturally friable rock. The larger crystals break away readily from the surrounding material, with little adhering gangue when this type of rock is mined. This is largely true also of the harder types of rock. Considerable hand cobbing, however, becomes necessary. The preparation of the crystal corundum may stop at this stage, although the resultant marketable grade obtained may sometimes contain less than 50 pct of the total corundum content

of the original ore. Further steps, however, may consist of rather primitive hand crushing or stamping with a steel rod and barrel cleaning or tumbling the crude hand-cobbed or sieved material. The latter method is the most generally used for cleaning corundum from reef deposits. If the rock to be treated is friable, as in corundum-bearing micaceous gneisses, a beater mill may be used. Cleaning not only is quicker with this type of equipment, but larger tonnages of ore can be run through. Boulder corundum, on the other hand, requires no treatment other than breaking up into pieces about one cubic foot or less in volume, or small enough to be conveniently handled. This may be accomplished by hand sledging or by hand drilling and blasting, followed by further reduction by sledging, if necessary."

Prior to World War II, milling was attempted at two periods, in 1922-1923 and in 1930-1931 at mills erected near Bandolierkop. Both attempts were unsuccessful, owing in part to concentrating difficulties and in part to the wide variability of the ore, which came from many different sources. In 1941 a mill was built at Pietersburg, which is still in operation. In 1945, a mill built at Turkapost in 1944 was operated by the U. S. Foreign Economic Administration. Metcalf⁸ states:

"Although 300 long tons of concentrates were produced from sub-marginal ore during 10 months' operation, the plant did not reach the efficiency anticipated. The crushing methods used at the plant did not provide the necessary liberation of the corundum from the gangue. The Foreign Economic Administration tried finer crushing of the ore and demonstrated that a 70 to 75 pct recovery in the form of a concentrate containing 85 pct corundum could readily be obtained by jigging. Capacities, however, were low, as most of the ores had to be crushed to minus $\frac{1}{8}$ inch."

No flowsheet of the Pietersburg mill is available for the present writing, but it is reported that the Turkapost experiment assisted in improving this mill both as to output and as to quality of product.

"No large corundum reefs of sufficient size and grade, such as would support even a 25-ton daily-capacity plant for any considerable time, are known to exist, but throughout Northern and Eastern Transvaal are many small deposits, containing 20 to 50 pct corundum, the ore from which could be transported by truck and rail to centrally situated concentrators. At \$103 per long ton, an economic production in excess of 3000 tons per year of concentrates (excluding boulder) could be maintained for several years. Any future emergency involving corundum will probably have to rely on this source."

Canada

Corundum was discovered in Canada in 1876 in Raglan Township, Renfrew County, Ontario. There are three recognized belts. The main

belt of corundum-bearing nepheline syenites is approximately 103 miles long, with some interruptions, and has a maximum width of 6 miles stretching through Renfrew, Hastings and Haliburton Counties, Ontario. The middle belt, in Peterborough County, 25 miles to the south, is a club-shaped area about 8 miles long and $1\frac{1}{2}$ miles wide at the head. The southern belt, in Frontenac and Lanark Counties, 65 miles east of the middle belt, is about 12 miles long by 2 miles wide.

Prospecting has been carried out in about 50 different localities but the principal operations have been at Craigmont, in Raglan Township, at the Burgess mine, Carlow County, and Jewelville mine, Radcliffe Township, all in the main belt. A small tonnage has been produced from Methuen Township, in the middle belt. The Canadian mineral usually is brown to bronze but an interesting deposit of blue corundum occurs on the York River, in Dungannon Township. Full details of the Canadian corundum deposits and operations are given in the Department of Mines reports.²

During the period 1900 to 1921, Canada was a regular producer of true corundum and for many of those years was the world's leading producer. The peak was reached in 1906 and 1907, when 2500 and 3000 tons of graded grain were sold. During the last three years of production, the corundum was obtained as concentrate from treating the old tailing dumps. The total output during the 21 years amounted to 20,422 tons of graded grain valued at \$2,104,251.

There was no formal production from 1921 until late in 1944, when a plant built by the U. S. Foreign Economic Administration to re-treat mill tailings from the old mill at Craigmont, Ontario, started operations. The tailings, averaging 2.96 pct corundum, were treated by grinding in a rod mill, screening and classifying concentrating sized feeds on Wilfley tables and cleaning concentrates with a Crockett magnetic separator. Up to December 1945, out of a total of 69,359 tons milled, 1397 tons of concentrate was recovered (43.7 pct extraction). Concentrates averaged 65.8 pct corundum.¹³

India

"Deposits of corundum are widely distributed throughout India.⁹ Although total reserves are said to be large, for the most part actual mining of abrasive corundum has been limited and often is done by local herdsmen or farmers. No systematic mining operations exist in most areas. However, considerable trade has been carried on for many years, particularly in the bazaar cities, such as Agra, Delhi, and Jaipur. The corundum sold by producers to agents of dealers in the larger cities is utilized by armorers and lapidaries.

"Deposits have been worked more or less regularly in the Coimbatore and Salem districts of the Presidency of Madras, at Golhushully and

Kulkairi in Mysore, in Kashmir, in the Khasi Hills in Assam, in Rewah Province, and in Hyderabad. Other provinces and native states said to contain more or less extensive deposits are Bengal, Burma, Central Provinces, Punjab, and Travancore. Corundum usually occurs as crystals disseminated throughout gangue rock, such as weathered syenites and schists containing pegmatite inclusions, diorites, peridotites, and others."

During World War I, production reached 2000 long tons but dropped back to nearly zero in 1922–1923. During World War II, an effort was made to increase production and new deposits were sought, but with little success. In 1942, production was 133 long tons and in 1943 was 88 long tons. While reserves are reported to be large, costs are very high because of the extreme inefficiency of local hand labor, inadequate transportation and lack of mining and milling equipment.

Madagascar and Russia

Madagascar—Corundum occurs in a soft, decomposed siliceous rock, which forms the so-called "red earth" that covers a large part of the surface of the island of Madagascar; sometimes to a depth of 60 ft. In places this earth has been washed from the summits and sides of hills, leaving the heavy minerals such as corundum, which are concentrated at the bottoms. Typical deposits occur in the southwest of Ambositra and also at Maovatanana and Betafo. The mineral usually is opaque and bluish in color, showing mica incrustations. Production since 1910 has been dwindling; the maximum of 800 tons occurred in 1919 and production fell steadily to 9 tons in 1931. Mining operations were renewed toward the end of 1935, when 12 tons was exported and production was maintained on a comparatively large scale in 1936. In 1945, production was estimated to range from 10 to 15 metric tons per month.

Russia—Small lenses of coarse-grained corundum occur in the western part of the Ilmen Mountains near the town of Kyshtym, Russia. The deposits were worked during World War I and considerable tonnage of the mineral has been mined in later years from near Lake Tscherkakul, in the Bajan-Aul division of the Pavlodar district. No details of production or methods are available.

EMERY—UNITED STATES

Emery is known to occur at a number of places in the eastern United States but it has been mined only from Chester, Massachusetts; Peekskill district, New York, and Whittles, Virginia, and for many years the production has come from New York.

For many years prior to World War II, production of emery in the

United States amounted to only a few hundred tons per year and in 1938 there was no production. With the start of the war in Europe, production rose steadily, from 765 tons in 1939 to 7856 tons, valued at \$75,977, in 1945—the largest amount since 1918. This great increase undoubtedly was caused by the cutting off of imports from Greece and Turkey, which in normal times amounted to 5000 to 7000 tons per year. Production in 1946 was 6188 short tons valued at \$62,099 and in 1947 was 5798 tons valued at \$66,927.

Massachusetts—Emery was discovered in Hampden County, at South Mountain, near Chester, Massachusetts, in 1864 by Dr. H. S. Lucas, although 30 years previously the deposit had been unsuccessfully worked as an iron mine. Previous to 1913, almost all the emery from the United States was produced from that locality. The deposits are associated with a narrow band of amphibolite, which extends almost continuously across the state. In the vicinity of Chester this band is about $\frac{3}{4}$ mile wide and the emery deposits can be traced for about 5 miles. The deposits occur in the form of a vein in the eastern side of the band, in close proximity to sericite schist. The emery is found in pockets from a few feet to 12 ft wide and has been mined in places to a depth of 300 ft. Six or seven mines were operated along this vein and large quantities of ore were extracted, but the workings have been abandoned since 1913.

Virginia—A spinel emery occurs to the west and south of Whittles, Pittsylvania County, Virginia. Although the deposits were exploited many years ago for iron ore, they were not successfully worked for an abrasive until 1917. For the next 11 years they yielded a large quantity of good material but there has been no production in recent years.

There are two types of occurrence: (1) schist ores, in which thin bands of quartzite, interbedded with the schists in places, form one, and sometimes both, walls of the emery bodies; the rock being closely jointed and in many places pegmatite; (2) granite ores, or those enclosed in a decayed granite, which often is cut by narrow pegmatite dikes. The emery in both types is a heavy, black, fine-grained crystalline aggregate. Weathering has progressed to an advanced stage, so that in all the ore deposits the rocks are entirely decomposed, and, owing to alteration of the schists into varicolored mottled clays, the surfaces of the emery bodies are often coated with a deep red clay. The ore bodies occur as irregularly shaped lenticular masses of solid emery, the largest of which is about 130 ft long and 6 to 8 ft wide.

New York—Emery deposits of the spinel variety occur east of Peekskill, Westchester County, New York, and have been operated by various companies since 1883.⁵ The ore occurs on the border of an igneous complex composed of hornblende and olivine pyroxenite termed the "Courtland" series. The emery occurs in a region in which mica-schist

inclusions are abundant, and is in sharply defined veins immediately associated with rocks containing sillimanite, cordierite, garnet and quartz. A characteristic of these schist inclusions is the great abundance of biotite found around the ore in many places. The two chief mines, the Dalton and McCoy, are worked by opencut methods.

EMERY—FOREIGN COUNTRIES

Greece—The island of Naxos is principally made up of gneisses and mica schists alternating with crystalline limestones. The lenticular masses of emery, varying in width from 15 to 150 ft, and sometimes as much as 100 yd long, are closely associated with the limestone. The best Naxos emery is dark gray, usually mottled with bluish specks or streaks of pure corundum, and is the hardest emery known. The best ore comes from Vothrie, 9 miles from the coast, on the northeast side of the island. Another important deposit is at Apiranthos, 7 miles inland, from which the ore is shipped at the ports of Sulinos and Mutzoma. On the northern part of the island it is mined near Yasso.

Emery of a similar mottled appearance and quality but of lamellated structure occurs on the island of Nicaria and a dark blue emery is found on the island of Samos, near the Asia Minor coast, but these deposits are not so extensive as those of Naxos. The mineral is sometimes also found embedded in white marble.

Turkey—Emery is obtained in Asia Minor from the province of Aidin, which embraces almost the entire basins of the Sarabat and Mender Rivers. Smyrna is the principal port and center of trade for the surrounding districts and islands. Railways extend from the city into the interior along the basins of the two rivers.

The greater part of the region is underlain by pure white or finely granular crystalline limestones, which are interfoliated with chloritic and micaceous schists and gneisses. The emery deposits occur as pockets or lenticular masses in the limestones and vary from a few feet to 200 ft in width and up to 300 ft in length. The mineral also occurs as a detritus resulting from the weathering of the rocks.

Extensive deposits have been worked on the Gumuch-Dagh mountain in the vicinity of Ephesus and from the slopes of Ak Sivri, which is about 100 miles southeast of Smyrna. The emery from the former locality is usually fine grained and dark blue to purplish in color while that from the latter deposits is coarse grained and much darker. The interior of the masses from the Gumuch-Dagh mountain deposits is free from micaceous inclusions. Kayabachi is at present the center of a number of small producing mines, the ores from which are shipped from the port of Kulluk. Other centers are Thyra, Aphrodisia, Inai and Azizieh, for which the shipping point is Smyrna. The ore exported is branded according to these seaports.

Usually the emery ore contains numerous fractures or cleavage planes, so that it is easily broken into blocks of suitable size for handling. The main source of supply has been the loose emery or boulders embedded in a compact red clay, which occurs in shallow depressions in the limestone.

Russia—In Russia, four deposits of emery, some of which are being worked, occur in the southern portion of the middle Urals northeast of the Kyshtym works, on the eastern shores of Irtyash Lake. At the southern end of the lake is the Techensky crushing mill. All the emery deposits are confined to bands of crystalline limestones in contact with granitic gneiss, and occur therein as lenses or bodies ranging in length from 15 to 100 ft and having a maximum depth of 150 ft below the surface.¹⁴

Other Countries—A small output of emery has been maintained annually from Wildenreuth, Bavaria. Emery occurs in several localities in Australia, mainly near Crookwell, New South Wales; also in the West Kimberley district of Western Australia. A fine-grained emery occurs in the Department of Minas, Uruguay, and also near Deschnet, eastern Fars, Persia (Iran), but no production from these localities has been reported.

Preparation for Market

EMERY

All the Greek and Turkish emery is shipped in lumps ranging in weight from a few ounces (lumps the size of a marble) to 25 lb.

In the United States there are several emery-crushing and grading mills in which the crude ore, both American and imported, is first crushed by jaw crushers and thence through a series of chilled rolls to $\frac{7}{8}$, $\frac{3}{8}$ and $\frac{3}{16}$ -in., then to finer sizes in ball mills. The mica is removed by allowing the coarse grain to fall down a chute; an uprushing current of air blows the mica to one side into a separate compartment. The emery then passes over a series of long troughs, shaking screens, whereby it is carefully graded into about 30 different sizes. The oversizes are further reduced by means of small rolls and return through the circuit.

In some plants the crude grain is washed with water in pans of the Chilean mill type, in which hardwood wheels revolve. This cleans off the adhering dirt and the cleaned material is dried and graded. Although this washing process is more costly, a much purer and better cutting article is produced. The overflow from the washing pans, containing all the fines, flows through a series of long settling troughs. The settled material is then shoveled out into drying ovens and this "flour" is further screened into three or four grades. The finest flour grades are made by drawing off the solutions at certain intervals of time and dry-

ing the residue after final settlement. The 12 sizes from 6 to 46-mesh are termed "coarse-grained" and the 12 sizes from 54 to 220, "fine-grained," and there are four "flour" grades, from F to FFFF. There are also still finer flours, produced by decantation methods, which are used principally for optical work.

In the manufacture of emery paper or cloth, the largest size is No. 4, or 20-mesh, and the following grading has been adopted:

Grade.....	4	3½	3	2½	2	1½	1	½	0	2/0	3/0	4/0
Mesh.....	20	24	36	46	60	70	80	90	120	150	180	220

The finer grades of paper keep their designation of multiples of F. In recent years acid treatment and roasting of the grain has considerably improved its abrasive qualities.

Specifications, Marketing, Uses and Prices

CORUNDUM

Specifications—For abrasive purposes corundum should have a bright and glassy luster and not be dull; the broken grain should be angular, uneven and sharp, not smooth or even; cleavage or parting planes should be absent, or nearly so; there should be no inclusions of other minerals; as a general rule the large corundum crystals are better than the very small ones.

During the latter part of 1945, exports of corundum from South Africa were limited, wherever possible, to the following:

CRYSTAL CORUNDUM—In grades designated A-1, A-2, B-3, and C-4, originating in the Transvaal, Namaqualand, Nyasaland, or Tanganyika.

CORUNDUM CONCENTRATES—Processed through milling, jigging, or other devices in concentrating plants, acceptable to the American Abrasive Co. as crystal grade.

BOULDER GRADE—All corundum ores and concentrates containing less than 85 pct and more than 70 pct Al_2O_3 .

CRYSTAL AND CORUNDUM CONCENTRATES—Crystal and corundum concentrates shall have a specific gravity of not less than 3.70, a minimum of 85 pct Al_2O_3 , a maximum of 10 pct SiO_2 , and a maximum of 5 pct Fe_2O_3 . Shipments are to be made according to the South African system of grading; all eluvial corundum to be separately bagged.

The South African system of grading refers to the Government-controlled regulations regarding sizes and grades of crystal corundum. These regulations, based upon total alumina content and designated screen limits, are as follows: A, not less than 92 pct Al_2O_3 ; B, 90 to 92 pct Al_2O_3 ; C, 85 to 90 pct Al_2O_3 ; and D, less than 85 pct Al_2O_3 . Sizes are classified according to the following scheme: (1) coarse,

$\frac{1}{2}$ -in. diameter and over; (2) medium, $\frac{1}{4}$ to $\frac{1}{2}$ -in. diameter; (3) fine, $\frac{1}{8}$ to $\frac{1}{4}$ -in. diameter; (4) mixed (M), $\frac{1}{8}$ -in. diameter or over. All these sizes are determined on a round-hole screen.

The grades most in demand by the American trade would be described as follows: A-1, a minimum of 92 pct Al_2O_3 and diameter of $\frac{1}{2}$ in. or over; A-2, a minimum of 92 pct Al_2O_3 and diameter of $\frac{1}{4}$ to $\frac{1}{2}$ in.; B-3, a minimum of 90 pct Al_2O_3 and diameter of $\frac{1}{8}$ to $\frac{1}{4}$ in.; and C-4, a minimum of 85 pct Al_2O_3 and $\frac{1}{8}$ in. in diameter and over. As shown, C-grade material occasionally is exported, but generally corundum of this classification is a "degraded" product; i.e., portions of shipments found not to come up to specifications.

Marketing and Uses—In service, South African corundum breaks down gradually and continually presents a new series of sharp-edged facets during the life of the individual crystals. The grinding surface, therefore, is always clean and fresh, which results in cooler grinding action. This advantage is most apparent with the coarse-grit vitrified-bond wheels, such as are commonly used in the snagging of steels and annealed malleable iron. Also, a definite advantage exists in lower grinding costs. Because of the cooler grinding, there is less breakage from heat, and the occupation is made less hazardous to the operators.

This feature of new and fresh grinding surfaces also has exceptional value in the grinding and polishing of optical instruments and lenses, as it allows the manufacture of the velvet-smooth and scratch-free glass and instrument parts that are essential in delicate optical equipment.

During the war, consumption of corundum was limited to the two uses just mentioned. For the optical grain, clean and graded material was prepared in some 13 mesh sizes, as follows: 60, 70, 80, 90, 100, 110, 120, 150, 180, 220, 240, 260, 275. The size limits of each grade are maintained carefully for both optical and wheel grain. The wheel-grain classification included 11 mesh sizes, as follows: 8, 10, 12, 14, 16, 20, 24, 30, 36, 46, 54.

Virtually the only importer of corundum during the war was Watson, Geach and Co., Inc., New York. The supplier was the Ore and Metals Co. (Pty.) Ltd., Johannesburg, South Africa, the firm handling the corundum export business for the Gifter Corundum Co. The Gifter Corundum Co. at present is the only large company in the corundum industry in the Union of South Africa. In addition to its own output, it purchases virtually all of the corundum produced in other operating areas in Africa. The corundum received by Watson, Geach and Co. was shipped to the American Abrasive Co., Westfield, Massachusetts, for reduction, sizing, and marketing. Another American firm occasionally importing corundum is E. J. Lavino and Co., Philadelphia, Pennsylvania.

Prices—There are no quotations on imported crude corundum.

Corundum grain was quoted in August 1948 as follows: per pound grain size 8 to 60 inclusive, $8\frac{3}{4}$ cents; 70 to 275, $9\frac{3}{4}$ cents; 500, 30 cents; 850, 45 cents; 1000, 45 cents; 1200 to 1600, 65 cents; 2600, 70 cents.

EMERY

Specifications—The specifications for an emery depend upon the uses to which it is to be put. Pure corundum or manufactured abrasives are considered too hard or harsh for certain grinding and polishing operations and it is the softer constituents of emery that tone down the harshness of the admixed corundum and give the desired results. The emery should contain corundum, that having the higher proportion being best suited for grinding wheels and that with the lower proportion for polishing and for pastes. The emery for the former should be hard and tough whereas for the latter a more friable emery gives a smoother finish.

Marketing—The sale of Greek or Naxos emery is under government control and buying usually is effected through agents on a commission basis, which includes the making of all shipping arrangements. The buyer pays the costs of weighing and lighterage, which average 4s 6d per ton. Exports of Naxos emery prior to World War II were mainly to The Netherlands, although there was a fair tonnage to France, Italy, and the United States.

For many years there has been more demand for Turkish than for Naxos emery, except in 1931, when the introduction of the acid-treated and heat-treated Naxos grain stimulated sales of the latter.

Uses—Naxos emery does not undergo detrimental physical and chemical changes under intense heat, and the grains are very hard and sharp, therefore this emery is the most suitable for the manufacture of grinding wheels. The Turkish emery usually is slightly softer than Naxos and the grains tend to break down under pressure. As it is fairly tough, it is best suited for the manufacture of emery cloth or paper, in the setting up of polishing wheels, and in pastes and compounds. In finer sizes the loose grains, both Naxos and Turkish, are used in grinding and beveling of glass. There are, however, some deposits in Turkey that contain an emery said to be harder than Naxos and to be usable for manufacture of grinding wheels. The American emery, being appreciably softer than either, is now used mainly in pastes and compositions. Considerable amounts are used as a nonslip, wear-resisting component in concrete floors.

Prices—Domestic crude emery ore first grade was quoted in August 1948 at \$12 per ton f.o.b. New York. Turkish and Naxos grain emery was quoted at 10 cents per pound in 350-lb kegs f.o.b. Pennsylvania. The domestic price was $6\frac{1}{2}$ cents.

GARNET

The name "garnet" is given to a certain group of minerals possessing similar physical properties and crystal forms, though their chemical compositions vary widely. The term is derived from the latin word *granatus*, meaning seedlike, because the crystals embedded in the matrix usually resemble seeds. Before the eighteenth century, the mineral was known as "granat."

Composition

The garnet group comprises seven different species, all of which are silicates of aluminum, calcium, iron, magnesium, manganese or chromium, the different metals being replaceable one by the other. Because of the variety in their compositions, some garnets are unaltered by weathering while others become completely disintegrated. Very often other minerals, particularly quartz, mica and pyroxene, are included within the garnet crystals, and in some instances these are so finely disseminated that it is almost impossible to make a mechanical separation of the garnet. Varieties of garnet are as follows:

Almandite ($3\text{FeO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$), the commonest, and andradite ($3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2$), also quite common, range in color from deep red, brown to black. The colored varieties of andradite are melanite (black), demantoid (green), topazolite (yellow-green).

Grossularite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$) may be white, pale green or yellow.

Uvarovite ($3\text{CaO} \cdot \text{Cr}_2\text{O}_3 \cdot 3\text{SiO}_2$) is emerald green.

Pyrope ($3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) ranges in color from deep red to black.

Spessartite ($3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$) is brown to red in color.

Rhodolite, a mixture of two molecules of pyrope to one of almandite, varies from pink to dark red.

Properties

COLOR—Color is outlined above under different varieties.

HARDNESS—Hardness varies from 6 (grossularite) to 7.5 (almandite, uvarovite and rhodolite), though some varieties of almandite are said to be 8.

CRYSTAL SYSTEM—Cubic, commonly as rhombic dodecahedrons or tetragonal trisoctahedrons, or in combination of the two.

CLEAVAGE—Occasionally an indistinct dodecahedral cleavage is observed, but some species of almandite possess a pronounced laminated structure, which forms planes of weakness along which the mineral separates, but this parting has no relation to the crystal form and is not a true cleavage.²⁰

FRACTURE—Garnets having a glassy structure usually have a marked conchoidal fracture but sometimes the mineral tends to break

into thin flakes (which probably are parting planes); in other varieties the fracture is sharp and uneven.

INDEX OF REFRACTION in grossularite is 1.735; almandite, 1.778 to 1.830; andradite, 1.865 to 1.94.

FUSIBILITY—High-iron garnets readily fuse to a dark glass almandite at 1315°C. High-chromium garnets are unfusible before the blowpipe.

TENACITY—Aggregates of crystals, or the laminated varieties, fracture readily into their component parts, but the solid and well formed crystals are very tough.

OTHER PROPERTIES—Specific gravity of garnets is 3.5 to 4.2; luster, vitreous resinous or dull; transparent to opaque; streak, white; dispersion, 0.24 to 0.28. Molecular weight: pyrope, 405; almandite, 499; andradite, 509.

Origin and Mode of Occurrence

Garnets occur as accessory minerals in a large variety of rocks all over the world but are particularly common in gneisses and schists. In some instances they are present in such large quantities that the rocks are designated as garnet schists or gneisses. They also occur as contact-metamorphic deposits in crystalline limestones, pegmatites and serpentines and other rocks. The usual associated minerals are hornblende, mica and quartz, with feldspar and pyroxenes in smaller proportions. Little information is available as to the occurrence of garnet below 400 ft in depth, because nearly all garnet mining has been confined to opencut methods, although garnet is sometimes found in the gangue at moderate depths in mining other ores; for instance, iron and copper. Garnets occurring in contact-metamorphic zones, which are formed by the replacement of the sedimentary rocks, are of secondary origin, but it is probable that the garnet in pegmatites and granites is one of the original rock minerals and of primary origin.

Because they are more resistant to weathering and erosion than their associated rocks, the garnets often occur as a detritus of crystals in the immediate vicinity of the original rocks, or as rounded grains in river and sea sands. In sands, owing to their comparatively high specific gravity, the garnets usually are concentrated by water action into beds or layers.

Garnets vary greatly both in size and in concentration. The crystals may be several feet in diameter—like those sometimes mined in New York state—down to crystals smaller than a pin's head. They may occur very sparsely distributed or close enough to constitute 70 pct of the rock. In some places there is high concentration of very small crystals as pockets or lenses and in others the garnet is in the massive form that does not disintegrate or break up into individual crystals.

Distribution of Deposits and Production

While garnet is a common constituent of rocks, large workable deposits of garnet with the most essential abrasive properties are scarce. Important commercial production has been largely confined to the United States and even here successful operations on an important scale have been predominantly in one area in New York state. The quality of New York garnet, hardly duplicated in any other area, is due to an unusual if not almost unique crystal property. This almandite garnet has incipient lamellar parting planes, which cause it to break, under pressure, into thin, sharp-edged plates—a most important property for garnet paper and cloth. Tough grains, whether of massive garnet or in small crystals, may be suitable for less important uses but are not acceptable substitutes for New York garnet.

This fact, together with the relatively small world demand, and the competition from artificial abrasives, has greatly restricted the search for and development of deposits of abrasive garnet.

The production of garnet in the United States reached an all-time peak of 9006 short tons in 1923. It dropped to 1950 tons in 1932 but recovered during World War II to 6306 tons, valued at \$375,198 in 1945, the highest since 1928. In 1946 production amounted to 7743 short tons, valued at \$570,186 and in 1947 to 8722 tons valued at \$614,071.

Imports have been negligible. Japan reported production of around 3500 tons per year of “garnet sand” between 1922 and 1925 but no information is available as to more recent production or as to quality of product.

India, Canada, Spain, Madagascar, Czechoslovakia and the Union of South Africa have been small, intermittent producers.

UNITED STATES

In the United States production in recent years has been confined to New York, Idaho, and North Carolina; but in years past New Hampshire, Vermont, Connecticut, Pennsylvania and Alaska were small producers. Deposits of possible value have been reported in numerous other states; for instance, Virginia, Georgia, and California.

New York

In 1945 there were only two producers in New York, The Barton Mines Corporation at North Creek and the Estate of John Burnham at Essex. The Barton deposit has been described by Vogel²⁶ as follows:

“The property is on Gore Mountain, 5 miles west of the village of North Creek, New York, and 11 miles by road. The altitude of the mine is approximately 2800 ft.

“The valuable mineral, garnet, occurs in a surface deposit, the ore

body being about $\frac{3}{4}$ mile long and varying in width from 50 to 300 ft. The garnet, principally almandite, $\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$, occurs in a metamorphic rock of uncertain origin. The gangue mineral is principally hornblende, which constitutes from 40 to 80 pct of the rock. The remainder of the gangue is divided between plagioclase feldspars and hypersthene, with smaller amounts of biotite, apatite and pyrite. The garnet content of the ore body varies from 5 to 20 pct of the mass and averages about 10 to 12 pct. The garnet occurs as crystals, mostly imperfectly developed, known locally as "pockets." These crystals vary in size from a fraction of an inch to a foot or more in diameter. Occasionally crystals have been found up to 30 and 36 in. in diameter but they average 4 to 6 in.

"Nearly every crystal of garnet is surrounded by a rim of coarsely crystalline hornblende. The quarry faces are striking in appearance, showing crimson-red garnet crystals with their coal-black rims scattered over a grayish black background. The specific gravity of the garnet is 3.8 to 4.1 while that of the hornblende ordinarily is 3.07 to 3.24. Some specimens of very dense hornblende have been found with a specific gravity as high as 3.40.

"The garnet crystals are laminated in structure and readily cleave into flat, tabular pieces with sharp, chisel-like edges. Even when crushed to a very fine size, the garnet retains this flat, sharp, slivery grain shape. This characteristic, together with its hardness and toughness, gives it its value as an abrasive."

The garnet rock is removed by quarry benching methods. While the deposit has been worked for more than 60 years, the garnet was recovered by hand cobbing until 1923, when the first mill was built—rebuilt in 1928. As the ore became leaner and more difficult to mill by jigging, a new mill, using sink-and-float or heavy media separation, was designed and placed in operation in September 1941. This mill, using ferrosilicon for the heavy medium, has been very successful.

The details are given by Vogel in the work cited. During World War II it was reported that superfine grinding equipment was installed at the Barton mill to supplement shortages of corundum flour used in the precision grinding of optical glass.

Other New York operations, formerly productive but now closed—for instance, the North River Garnet Co., on Thirteenth Lake 10 miles from North River and Warren County Garnet Mills, near Weverton and Johnsburg—were described in the first edition of this book (AIME 1937) and in the literature.¹⁶⁻²⁷

Other States

New Hampshire—Near North Wilmot, New Hampshire, the garnet deposit formerly operated by the Wausau Abrasive Co. and Davenport

Garnet Co. has not been operated for several years. This has been described by Conant.¹⁷ The garnet, in crystals $\frac{1}{4}$ to $\frac{3}{8}$ in. in diameter, constitutes 40 to 60 pct of the parent biotite-mica-feldspar schist. This garnet lacks the lamellar parting of the Barton garnet and the structure is somewhat weakened by minute intergrowths of gangue minerals.

North Carolina—In North Carolina for several years prior to 1942, Celo Mines Inc., at Burnsville, recovered abrasive garnet as a by-product of kyanite milling, and marketed a -20 +48-mesh product for sandblasting. There has been no production since 1942. The famous deposit of rhodolite garnet at Sugar Loaf Mountain, $2\frac{1}{2}$ miles south of Willets, North Carolina, was worked intermittently between 1900 and 1926 and two mills were built, the latest in 1925, but there has been no recent production. The garnet, in crystals up to nearly $\frac{1}{2}$ -in. diameter, occurs in quartz-feldspar-mica schist in concentrations averaging 20 to 25 pct but as high as 60 pct.

In Clay County, North Carolina, there are important almandite garnet deposits in hornblende gneiss at Pennland Bald, on Buck Creek, and on Shooting Creek, east of Hayesville. The deposits are reported to be large, with crystals up to $2\frac{1}{2}$ in. in diameter constituting an average of about 10 pct of the rock mass—as high as 25 pct locally—but they are unworked.

Idaho—From Idaho, in recent years has come a small production of garnet by several producers. This garnet sand is recovered by screening and classifying from stream gravels near Fernwood, in southeastern Benewah County, western Idaho.

California—California was reported to have produced a small tonnage of garnet in 1938 as a by-product from a tungsten mill near Bishop, Inyo County. It is stated that this was sold as a graded sand, at \$15 to \$20 per ton, for use as an abrasive by the aircraft industry. Numerous garnet deposits have been noted elsewhere in the state, as near Indio, Riverside County, but there has been no reported production.

FOREIGN COUNTRIES

Alaska—In Alaska, at Rothsay point, at the entrance of Stikine River opposite Wrangell, beautifully formed, almost transparent, claret colored crystals, $\frac{1}{2}$ to 1 in. in diameter, occur at fairly regular intervals in a fine-grained, dark gray mica schist. They are said to have good abrasive qualities and small shipments were made to the West Coast 20 years or more ago.

Canada—In Canada about 100 occurrences of garnet have been noted,¹⁸ but virtually the only production has come from a deposit in Ashby Township, Lennox and Addington Counties, Ontario. Here in 1923-1924 about 1200 tons of rough concentrate was produced and

shipped. Trial shipments have been made from deposits near Labelle, 100 miles north of Montreal.

Spain—In Spain alluvial deposits of garnet have long been worked in the Province of Almeria. The garnets are small in size and poorer in quality than the American but at one time imports into the United States amounted to 500 to 3000 tons per year, though these imports ceased in 1933.

India—In India numerous deposits of garnet are known and a few have been exploited in a small way, as in the Tinnevely district of Madras, Nellore in the Deccan and at several localities in Mysore.

Other Countries—Small and irregular shipments have been made from Madagascar. Tests have been conducted on garnet from deposits in Ceylon, South Africa, Malawe Hill in Nyasaland, British Somaliland, from an island in St. Huberts Bay off the Labrador coast, and other places. Near Prague, Czechoslovakia, alluvial garnet (pyrope) has been washed and concentrated in crude jigs. Mittleburge, Czechoslovakia, was at one time the world center for gem garnet, 10,000 men being employed.

Preparation for Market

Before being used for the abrasive coating of papers and cloths, the garnet must be concentrated and graded. Being a heavy mineral (avg sp gr 4.0), garnet is usually concentrated by ordinary gravity methods, either wet or dry. The former is the general practice and the more suitable for the majority of the ores. The main object in concentrating garnet for the paper trade is to obtain a material with as large a mesh and as pure as possible, and to avoid fines. The manufacturers of coated abrasives in the United States usually prefer to do their own grading (sizing), so they require coarse material from which varying proportions of any size can be obtained by crushing; but in crushing, fines are unavoidably produced. When standard grading is more general, these grades may possibly be made direct in the course of concentration, but the present practice in milling is to mix together and bag all the grades obtained. The degree and stages of crushing are of the utmost importance, therefore, and care must be taken that the coarse particles of garnet are free from attached impurities. Therefore it is necessary that preliminary concentration tests be conducted on a garnet ore in order to determine the most efficient degree and type of crushing before the erection of the mill. Details of garnet flow-sheets, machinery and concentration tests will be found in various reports.^{16,20,21,23,26}

Heat-treatment—The toughness, fracture and color of iron garnets are improved by heating the grain at about 800°C for about 12 hr and then quenching. This treatment, covered by U. S. Pat. 1836448, Sept. 22, 1930, and by U. S. Pat. 2029253, Aug. 30, 1935, is successfully em-

ployed by several manufacturers of abrasive-coated papers and cloths.

Grading—Grading consists of alternately crushing and screening the concentrate in order to obtain the full range of grades (mesh sizes) required by the manufacturers of sandpapers.

Tests and Specifications

QUALIFICATIONS OF ABRASIVE GARNET

Garnets vary considerably as to color, hardness, toughness and method of fracture. For the best abrasive, it should be as hard as possible, at least 7.5 (quartz is 7.0). When the garnet is crushed the grains should break into sharp, angular fragments with curved or rounded edges. The mineral should not break too easily but it should be brittle enough so that the individual grains eventually will break and form new cutting edges rather than become rounded under the strain of work. Thin or slivery grains do not arrange themselves correctly because they tend to lie too flat when applied to the glued surface of paper, thus presenting a smooth, noncutting surface, or they protrude above the surrounding grains and tend to scratch. The crushed garnet grains should have a high capillary attraction, so that the glue will completely cover and adhere to them when they are being fastened to the paper or cloth.

The color does not seem to have any particular bearing on the abrasive qualities, but the deep red or wine colored mineral is always preferred.

In order to obtain the full range of grades necessary for coated papers, the garnet should be capable of being broken into comparatively large (size of a pea), clean and solid pieces free from embedded impurities, and with the minimum amount of fines. Therefore deposits that contain garnets of small crystals are of little or no commercial value for sandpapers, no matter how great the garnet content of the rock may be. Granular garnet usually breaks into rounded grains; other deposits containing large crystals that are badly shattered, or crystals containing embedded impurities, would crumble almost to dust with little pressure. The compact, massive garnet might be used commercially but comparatively little experimental work has been done on that type. Massive garnet, however, is almost invariably off-color, and the toughness and hardness of the crushed grains are usually inferior to those of solid garnet crystals. The grains in garnet sands are too small and they are rounded by erosion and water action.

Briefly, therefore, the best abrasive garnet comes from deposits of clean, unfractured, individual deep red crystals at least the size of a pea but preferably larger. The recovery from the average types of

deposits should be at least 10 pct of such garnet in order to be commercially valuable. Up to the present, the highest quality of abrasive material has been obtained from the large, laminated crystals or boulders of red garnet like those in New York state. The kinds used for abrasive purposes are all iron garnets. Almandite is the commonest but andradite and rhodolite are also used.

TESTS FOR ABRASIVE UTILITY OF GARNET

There is no efficient method of testing the abrasive quality of garnet or of any other loose-grain abrasive. The real test is in its practical application. There are, however, several rough tests and examinations that serve to indicate their abrasive possibilities. The size, fracture, shape and purity of the grains, as outlined in the foregoing paragraphs, can be determined or compared by the microscope. The *toughness* of different garnets may be roughly compared by reducing them to the same grade (No. 1) and drawing a knife blade over a small quantity placed on a piece of steel or glass. Soft garnets will drag and soon break up into powder, but the knife will ride over the tough particles without appreciably reducing their size.

CAPILLARITY

The capillarity test is made on crushed garnet and serves to indicate its tenacity when applied to the glued surfaces of the paper or cloth. The higher the capillarity, the tighter will each particle adhere when coated with glue. Capillarity testing methods are described by Eardley-Wilmot.¹⁶

TESTING MACHINES

The only real test for garnet for coated abrasives is the rate at which it will abrade wood when compared with a standard sample. Since the nature of adhesive used and method of applying are nearly as important as the quality of the grain, samples should be prepared by experienced manufacturers. The test consists of abrading wood blocks in a drum sanding machine, with both standard coated paper and that to be tested, and comparing loss in weight of the blocks.

Marketing, Uses and Prices

Probably about 90 pct of the abrasive garnet is used for the manufacture of abrasive-coated papers and cloths and the remainder as a lower priced material in the form of loose grain for various purposes, such as surfacing and polishing marble, slate, soapstone, and other soft stones; in some sandblast operations and a very small amount for the surfacing of plate glass.

ABRASIVE PAPERS AND CLOTHS

On the American continent garnet-coated papers and cloths are used in the woodworking industries, particularly for hardwoods. In abrading softwoods, garnet and quartz papers appear to be nearly equally efficient, as both are soon clogged with particles of wood; consequently there is no advantage in the higher priced garnet. The recent introduction of open-coated papers, however, largely overcomes this trouble. In hardwoods the superiority of garnet over quartz is most pronounced and the cutting efficiency of the former is said to be from two to six times that of the latter. These papers are used also for the finishing of hard rubber and celluloid, for felt and silk hats, and as fine disks in dental work. They are employed extensively on leather, particularly in the boot and shoe industry for the scouring of heels and soles. In recent years fine grits of waterproof garnet papers have taken the place of pumice in the rubbing down of varnished and painted surfaces, especially automobile bodies. Garnet cloths are sometimes used for the softer metals.

The garnet-coated abrasive is used in the form of belts, covers for drums, disks, and as small sheets in hand work. The different grades of garnet used on these papers and cloths range from No. 5, the coarsest, which is about 15-mesh, to 7/0, which is about 220-mesh.

Details of the manufacture of coated papers are given in part IV of the Mines Branch Abrasives report.²⁸ The recently introduced method of electrostatic coating is meeting with success. In this process an electrostatic machine causes the grain to jump up and embed itself in the wet, glued surface of the moving backing. It is claimed that the grains stand up on their edges and are more evenly surfaced, owing to individual grain repulsion. This is a distinct advantage over the old method of coating, particularly if flat or slivery grains are present.

LOOSE GRAIN

A small amount of garnet grain is bonded into wheels made by low-temperature processes that are employed for grinding glass and some metals. Some sales are made annually within the United States and Canada of crushed and sized garnet ore for sandblasting stone monuments (inscriptions) and certain metals. A good, tough garnet from very rich deposits that would not require the expense of concentration might prove an efficient competitor of silica sand or of the more expensive metallic or manufactured abrasives.

Graded garnet grains are used to some extent for metal finishing; for example, 150 and 220-mesh in a grease vehicle for lapping softer types of iron and steel gears.

GLASS SURFACING

The excess fines produced in manufacturing abrasive coatings, as well as finely crushed and water-settled garnet ore, were utilized for some years in the United States for surfacing plate glass in the stage between the coarse sanding and the final rouge polishing. Garnet was introduced for this purpose in 1914 and between 1925 and 1934 a fair tonnage was consumed by the glass industry. The Ford Motor Co. was the largest user and operated its own deposit at Danbury, New Hampshire, solely for this purpose, but in 1935 the company discontinued this use of garnet and reverted to graded sand. It is believed that very little garnet is now being used for surfacing glass.

GEM GARNET

Clear, flawless garnets of various colors are extensively used for ornamental purposes. Between 1883 and 1920, the value of gem garnet produced in the United States varied from \$2,000 to \$22,000 in a year, the high values being obtained from the rhodolite garnet in North Carolina during 1900 and 1901. The output in the United States has dwindled to a figure so unimportant that no records have been kept since 1921. A large quantity of garnet is used for the jewels of the cheaper watch movements but none has been produced in America for this purpose except a small amount during World War I, because the foreign supply has been abundant and its prices lower than the cost of domestic production. Further details are given in the chapter on Precious Stones and also in the U. S. Bureau of Mines *Bulletin* 256.²³

MARKETS

While the demand for garnet has declined considerably since the 1923 peak of about 9000 tons, owing largely to its partial replacement by artificial abrasives, there is no reason to believe that it will decline much further, except as influenced by the general levels of industry.

In Europe, garnet is not so extensively used as on the American continent. This may be attributed to the inferior quality of the Spanish garnet, to the high price of the American, and to the use of chalk flint, which is cheaper than garnet and occurs in great abundance in England and in France. It is superior to the American so-called "flint" (which is really quartz) and is almost equal to garnet in its abrasive qualities. The European manufacturers of coated abrasive require graded grain whereas the American manufacturers buy most of their material in the form of concentrates and grade it themselves, although some graded grain is sold by the producers of garnet.

PRICES

Garnet concentrates, grain from the Adirondack region, New York, were quoted in August 1948 at \$85 per short ton.

GRINDSTONES AND PULPSTONES

Grindstones

The use of natural grindstones, along with that of many other natural abrasives, has declined greatly because of competition by artificial abrasives. Domestic production, which reached about 45,000 tons in 1920, declined rapidly to an average of around 10,000 tons per year for the past 15 years. Production in 1945 was 10,033 tons valued at \$399,565 and in 1946 it was 11,605 valued at \$501,444. Natural grindstones find their largest market in the manufacture of saws, knives and other thin-edged tools, because there is less danger of "burning" the steel.

Grindstones are made from sandstones in which the grains are bonded with silica, calcium carbonate or iron oxide. The quality of a stone depends upon the size of grain, shape of grain (sharpness of edges), and the amount and character of the cementing material. The value of a deposit is judged by the quality of the stone, the thickness of the beds, and the closeness of spacing of cross joints. It is essential that the deposit be able to yield large, sound, uniform blocks.

DISTRIBUTION OF DEPOSITS

In the United States, Ohio is the chief producer. Some production still comes from West Virginia, but the formerly important deposits in the Huron district of Michigan are not now operated.

In Ohio deposits of sandstones suitable for grindstones are widespread, from the northeast corner of the state west to Norwalk, 70 miles west of Cleveland and south to the Ohio River. Well-known "grit" names derived chiefly from producing centers are: Berea, Amherst, Independence, Massillon, Tippecanoe, Marietta and Constitution.

In Canada, where manufacture of grindstones was formerly important, the best deposits are in New Brunswick and Nova Scotia. The best known "grits" were the Bay of Chaleur from Stonehaven, New Brunswick, and the Joggins from Nova Scotia, but the industry is of little importance today.

In England the production centers have been Newcastle, Derbyshire and Yorkshire. The Craighleith grit from Scotland was formerly well known.

Pulpstones

The history of the pulpstone industry parallels that of grindstones and for the same cause, the increased use of artificial abrasives. From a

peak of 10,030 tons valued at \$750,063 in 1921, production has declined to less than 2000 tons in recent years, valued at around \$100,000.

It is easy to understand why artificial pulpstones have replaced natural stones when relative economy is considered. Heywood⁸⁸ states that "the life of a manufactured pulpstone can reasonably be expected to be 4 to 7 years as against 3 to 20 months for natural stones operating under similar conditions. Records of 67 by 54-in. manufactured wheels show costs ranging from 9 to 14 cents per ton of pulp ground. Natural stones under the same conditions cost from 30 to 35 cents per ton of pulp."

While pulpstones are made from sandstones similar to those used for grindstones, rarely does the same bed yield stones for both uses. Pulpstones, used for grinding wood fibers for papermaking, should be neither too fine nor too coarse, be of medium hardness, have a long life, wear evenly and withstand the strains.

Since modern pulp-mill practice requires large stones, up to 54-in. diameter by up to 67-in. face or larger, only thick, uniform beds of sandstone are suitable—beds at least 10 ft thick.

While formerly pulpstones were produced at numerous points in Ohio and in Washington (Rockport and Wilkeson), in 1945 production came only from West Virginia (Monongalia County).

In Canada production has come from Northumberland and Westmoreland Counties, New Brunswick, but more recently from Gabriola and Newcastle Islands off the east coast of Vancouver Island, British Columbia.

Quarrying and Finishing

While grindstones and pulpstones differ in size, production methods are similar. Formerly rectangular blocks of proper dimensions for grindstones or pulpstones were drilled and wedged out of the beds. These blocks were then cut to size in gang saws, corners rounded and turned to shape in lathes. By more recent practice cylindrical blocks of the desired diameter are cut in place in the bed, by means of cylindrical steel cutters, mechanically turned about a vertical axis and fed automatically. Split steel shot act as the abrasive. When a cut is completed to the desired depth the block is freed by drilling horizontal holes at the base and shooting with light charges of powder.

These blocks may be finished as single stones or sawed into several thinner pieces. Square holes are cut in the centers and the stones are trimmed, sides and face, in a lathe.

Proper seasoning of pulpstones is of great importance. Freshly quarried stones are saturated with water, which evaporates slowly, enabling the cementing material to harden. Seasoning requires from one to two years, depending on size of stone and fineness of grit.

MILLSTONES AND CHASER STONES

Nomenclature of millstones and chaser stones has become confused, owing to improper usage. Millstones originally were flat, round stones, rotated in a horizontal plane, used for grinding grain. Two stones were used, one above the other, one usually being driven and the other stationary. The stones were fluted radially to provide sharp cutting edges. Grain, fed from above through a central eye in the upper stone, worked its way out between the stones. This same type of mill was adapted to the grinding of minerals such as gypsum or talc and to paints.

Chaser stones were much larger and heavier circular stones, run on edge, turned by a central shaft on a pavement of hard, tough stone. A common size for chaser stones was 6-ft diameter by 18 to 22 in. wide. They were used to coarse-grind ores and minerals. In the preparation of nonmetallic minerals, where contamination from metal grinding surfaces was important, as in milling feldspar, quartz and barite, these mills were once commonly used. Today their use has nearly ceased. Improperly, chaser stones have often been called millstones.

Many years ago production of millstones and chaser stones in the United States used to reach a valuation of around \$100,000 per year. Recently this has dropped as low as \$3743 (1938) and the average for the past 10 years has been only about \$10,000 per year.

The best millstones were made from French buhrstone, a very strong, tough, cellular quartzite, as hard as flint but not as brittle, quarried in the Paris Basin, chiefly at La Ferteous-Jouarre. Quarried blocks of buhrstone were either shaped to proper size and sold as solid stones or fitted together and bonded into built-up wheels.

There is no true buhrstone in the United States but millstones have been made from quartz conglomerate (e.g., the famous Esopus stone from near Kingston, New York), from quartzite (e.g., from Brush Mountain, Montgomery County, Virginia), from sandstone (e.g., the Berea sandstone from Peninsula, Ohio); and from granite (e.g., from Faith, Rowan County, North Carolina). Chaser stones often have been made from granite.

In recent years the very limited production has come from Minnesota, New York, North Carolina, Virginia, and West Virginia.

SHARPENING STONES

The small hand-operated stones called sharpening stones include scythestones, whetstones, razor hones, oilstones, waterstones, holystones and rubbing stones. Their nomenclature is confused because there is no sharp line of demarcation between types, either in use or in texture and hardness.

They include a wide variety of natural stones as well as those made

by bonding grains of artificial abrasives. Natural stones include sandstone, mica schist, siliceous argillite, shale, slate, pumice, and similar stones. The superior cutting quality of some of these stones is due to well disseminated, fine-grained inclusions of garnet or other minerals of superior hardness.

The peak of U. S. production of natural sharpening stones in the last 20 years or so was 1680 tons in 1926, valued at \$223,359. From 1935 to 1939, production averaged 500 to 600 tons per year. Since then production statistics have not been published, but there has been no important increase. Just prior to World War II (1937-1939), imports ranged from 70 to 100 tons.

Scythestones

Scythestones include all stones used for sharpening scythes and sickles. The grit is also suitable for kitchen and butcher knives and similar articles. They are the coarsest of the whetstones and usually are made from the finer beds of sandstone from which grindstones are obtained. The better grades of scythestone are usually fine-grained, highly siliceous argillite or mica schist, which often contain, in addition to the quartz, innumerable minute crystals of some hard mineral such as garnet or magnetite.

Razor Hones, Oilstones and Waterstones

Razor hones embrace all stones used for sharpening razors and delicate instruments. At present most razor hones are made from artificial abrasives, although there is still quite a demand for the natural Belgian honestone.

Oilstones, as the name indicates, are very fine grit stones from which the most satisfactory service is obtained by the use of oil. There is a large demand for artificial oilstones, and large quantities of the opalescent, siliceous novaculite from Arkansas also are used annually.

Water is used with some stones, although very satisfactory results are obtained with oil. The best varieties for water are the Hindostan stone from Indiana and the Queer Creek stone from Ohio.

Holystones or Rubbing Stones

Holystones, which are made from blocks of close-grained sandstone, were at one time used extensively for rubbing down ships' decks and the name is said to have originated from the fact that the work was done in a kneeling position. The stones now are used to some extent for rubbing down rough surfaces on which a fine finish is to be applied, particularly automobile bodies, furniture, and concrete work.

Other rubbing stones include block pumice and Bath brick. The latter are made from a fine-grained, quartzose clay found along the banks of the Parrot River in England.

Other Sharpening Stones

While artificial abrasive stones have largely replaced the natural stones, there are still a few uses for natural stones of superior quality. One example is the Arkansas novaculite, which is still preferred to artificial abrasive stones for sharpening fine-edged instruments such as surgeons' and engravers' tools. It is claimed that these novaculite stones give a smoother and longer lasting edge.

Another example is "the Belgian³⁴ razor honestone (*coticule*), now imported into this country for use in sharpening razor blades and the microtome knives used in the preparation of microscope-slide specimens. The Belgian *coticule* is a regionally metamorphosed, argillaceous sedimentary rock occurring in the Ardennes in southeastern Belgium as thin, clear yellow to yellowish gray, compact, homogeneous, fine-grained beds $\frac{1}{2}$ to 3 in. thick, interstratified with blue-gray or violet Cambrian phyllites, in some places merging gradually into them but more often sharply distinct in coloring.

"Billions of tiny, nearly spherical, polyhedral, hard crystals of light yellow manganese garnet, spessartite, in a soft sericite matrix, form the principal element of the *coticule* and explain its yellow color, hardness, peculiar fitness for hones, and manganese content (17 to 22 pct MnO). The average diameter of these microscopic garnets is about 0.0008 in. Tiny rutile and tourmaline crystals also occur in the *coticule*. The mineral composition of the phyllite differs from that of the *coticule* in that hematite and carbonaceous matter are present.

"The beds of *coticule* and attached phyllite are cut in a characteristic manner. As the phyllite has abrasive qualities, part of it is left attached to the *coticule* to support it. The hones thus appear double-faced, with yellow *coticule* on one side and the softer blue-gray phyllite on the other."

Distribution of Deposits

UNITED STATES

In recent years production in the United States has come from Arkansas (oilstones and whetstones), Indiana (rubbing stones), New Hampshire (scythestones), and Ohio (scythestones, whetstones and miscellaneous).

Novaculite—Novaculite is a fine-grained and compact white, quartzose rock, supposed to be a consolidated siliceous slime. It consists almost entirely of chalcedonic silica (over 90 pct) and is of sedimentary origin. The rock is quarried principally from the vicinity of Hot Springs,

Garland County, Arkansas. There are two varieties, the true novaculite (Arkansas stone), which is white, and the Washita (Ouachita) stone, which in many instances has a yellowish or rusty red tint.

Arkansas stone is very dense and has a conchoidal fracture and waxy luster. It occurs in massive beds a few inches to 15 ft thick, in the novaculite formation, which has a total thickness of 500 ft and includes thin layers of shales and sandstones. As a result of pressure, the brittle novaculite has in many places been crushed and split; and, in addition, many fine quartz veins intersect the rock in all directions, some so thin as to be invisible to the naked eye. As these are detrimental, careful sorting is necessary, and the amount of waste is out of all proportion to the material eventually used. Large blocks of even apparently pure stone are not shipped but are broken into pieces weighing up to 5 lb. Freezing also has an injurious effect on this stone, as denseness of the stone does not allow for expansion.

Washita stone has approximately the same composition as the Arkansas but is less dense and more porous. It has a subconchoidal fracture and resembles unglazed porcelain. It is freer from defects than the Arkansas stone; quartz veins are not so numerous, but cavities or "sand holes" are much commoner. On account of its greater porosity, freezing does not have an injurious effect. Long drying is inadvisable, however, as it seems to cause loss of easy fracture and to make the stone tough and hard. The stone is less expensive than the Arkansas and is a faster cutting stone, but it is used for coarser work. The Washita stone is shipped in blocks weighing 50 to 1000 lb. It is found in much larger quantity than the Arkansas stone and the demand for it also is much greater.

Mica Schist—Fine-grained, dark gray, highly siliceous, laminated mica schist is quarried at Pike, Grafton County, New Hampshire. The quartz grains occur in definite layers separated by thin layers of mica. The part of the rock containing coarse, irregularly scattered quartz and argillaceous matter is discarded. There is a regular system of cross jointing at right angles to the bedding planes, so that after blasting slabs or "bents" are easily pried out. The irregular slabs are first roughly trimmed, then further reduced and stacked. The Pike quarries have been producing scythestones for more than one hundred years.

A bluish chocolate colored schist (known as "chocolate stone") was formerly quarried at Evansville, Vermont.

Sandstone—Among the better known of the sandstones is the Hindostan, or Orange stone, from French Lick and Northwest Township, Orange County, Indiana. Some of the crude material is shipped to Pike or Littleton for manufacture. It is a fairly soft, fine-grained, low-priced waterstone used mainly by mechanics and for domestic service. West Baden, Indiana, is also a producing center.

Scythestones have been manufactured by several of the Ohio grindstone companies, particularly from the Berea and Euclid grits. The Queer Creek stone is a hard, dark gray, medium coarse sandstone, which is used as a waterstone for coarse sharpening. The Euclid is a blue, very fine grit stone used mainly for butcher and pocket knives. The Berea grits are used for the coarsest work, and the Huron for medium.

OTHER COUNTRIES

Some of the better known foreign stones are:

SCOTCH HONE, also known as WATER-OF-AYR, SNAKESTONE, or TAM O'SHANTER, is a mottled, pale gray, compact stone from Bridge of Stair, near Dalmore, Ayrshire, Scotland.

"RAG-STONES," from Scotland, consist of siliceous mica schists having a twist along their length, which gives a sharp "bite."

CHARLEY FOREST or WHITTLE HILL honestone is a very fine-grained, hard tuff from Leistershire, England.

The IDWAL or WELSH OILSTONE and the CUTLER'S GREEN come from Snowden, Wales.

The BELGIAN HONESTONE has been described above.

The RATISBON honestone (Germany) is similar to the Belgian.

The SONNEBERG (Germany) water hone is a hard, fine-grained, bluish green argillaceous schist.

The SMYRNA (Turkey) oilstone is a novaculite similar to the Arkansas stone but is not uniform. Until the discovery of Arkansas novaculite, these stones, for several centuries, were considered the world's best for sharpening tools.

Manufacture

In New Hampshire, scythestones are split roughly to shape, ground to uniform size on rubbing beds using local sand as the abrasive, then trimmed to exact length and hand-finished.

Arkansas novaculite comes from the mines in relatively small lumps. These are built up with plaster of paris into larger blocks, which are cut by band saws into 2-in. slabs. Individual pieces from the slabs, reassembled with plaster, are again cut into 8-in. lengths. Finishing is on a horizontal rubbing bed with sand abrasive and the stones finally are recleaned with pumice. Smaller fragments are worked up into small special shapes, by sawing with diamond saws and grinding on the rubbing bed. Chips and waste are ground to a powder that is used by makers of watches and razor blades for polishing and grinding.

GRINDING PEBBLES AND TUBE-MILL LININGS

Tube mills, conical mills and cylindrical batch mills are used more often than any others for the fine grinding of hard ores, minerals, paints,

chemicals, ceramic bodies and glazes and enamels, portland cement clinker, and similar materials.

Most efficient grinding can be done in mills with iron or steel liners and iron or steel balls, slugs or rods, but where contamination of the color or chemical purity of the product by metals and metal oxides must be avoided, the grinding surfaces must be natural or artificial non-metallic mineral products. These grinding surfaces consist of blocks or bricks for the mill linings and natural pebbles or artificially prepared balls.

The requirements are that these materials have high abrasive hardness; great toughness and freedom from flaws, which will result in breaking and chipping; produce a white powder when abraded; and contain no dark colored metallic impurities such as iron or manganese. While most of the natural and artificial mill linings and pebbles have a specific gravity close to that of quartz (2.6), a greater density in pebbles has obvious advantages. The heavier the pebbles per unit of size, the greater are the impact and abrasive grinding forces. Thus, with heavy pebbles less mill volume is needed for a given pebble load (by weight), resulting in greater mill capacity; or with equal pebble volume, faster grinding can be done. Small balls grind finer than large ones (because of more surface area per pound), but with small pebbles the unit weight is low unless heavy-density pebbles or balls are used.

The most favored natural mill-lining material for most purposes is Belgian silex, which is a very hard, tough, more or less cellular quartzite resembling French buhrstone. This is imported in rectangular blocks more or less shaped to fit the curve of a mill. During World Wars I and II, when imports were cut off, and to a much lesser extent at other times, domestic substitutes have been used. These have consisted chiefly of quartzite from near Jasper, Minnesota, and Iron City, Tennessee, and granites from Salisbury, Lilesville and Faith, North Carolina, and Baraboo, Wisconsin. Some of these materials are reported to give service equal to that of Belgian silex. Special hard, dense, porcelain blocks are used in some mills for grinding paint, ceramic and chemical materials.

For grinding media, Danish flint pebbles, when available, have long been standard because of their superior hardness, toughness and uniformity. These pebbles are found on the shores of Greenland but are marketed through Denmark. Other foreign sources of similar pebbles are along the seacoasts of Belgium, France (between Havre and St. Valéry-sur-Somme), Norway, and England. Seven sizes of Danish pebbles are marketed, ranging in size from 1 in. to nearly 8 in.

As domestic substitutes, there have been used natural pebbles of flint, quartz and quartzite, as well as artificially rounded (by tumbling small blocks in rotating cylinders) pebbles made from quartzite, gran-

ite, chalcedonized rhyolite, and other rocks. During World War II, pebbles were shipped from Encinitas Beach, California (true flint); Jasper, Minnesota (quartzite); from the Edwards chalk beds in south central Texas (true flint); from Salisbury and Faith, North Carolina (granite); from Baraboo, Wisconsin (quartzite); and several other points in the United States. Extensive deposits of quartzite pebbles in southwestern Saskatchewan have been reported. Beach pebbles were imported from Newfoundland but were reported as nonuniform in hardness and requiring careful sorting.

Ceramic pebbles are made from very dense, tough, porcelain and sillimanite (mullite). A dense, heavy pebble is made from zircon, having a specific gravity of 3.7. For certain purposes blocks of ore are used as grinding media; thus nepheline syenite blocks are used instead of pebbles for grinding this material.

Because of the cutting off of imports during the war, the domestic production probably reflects nearly the total consumption in the United States under war conditions (Table 4).

TABLE 4—*Production of Tube-mill Liners and Grinding Pebbles^a in the United States*

Year	Tube-mill Liners		Grinding Pebbles	
	Tons	Value	Tons	Value
1941 ^b	3,411	\$54,216	13,561	\$221,826
1942	2,576	49,967	15,487	245,794
1943	2,585	46,071	9,924	157,778
1944	2,063	38,833	8,012	172,418
1945	1,982	45,933	8,615	201,806
1946	2,375	44,247	4,652	102,043
1947	1,496	40,203	5,860	122,883

^a Minerals Yearbook, U. S. Bureau of Mines.

^b Statistics for earlier years not revealed because of too few producers.

SILICA

Silica sand and quartz are reviewed in detail elsewhere in the volume, so that only their abrasive uses and applications are given here.

Silica Sand

Silica sand is extensively used for sandblasting, for the initial grinding or surfacing of plate glass, and as a cutting medium for gang saws on stone.

For sandblasting the main centers of production in the United States are Ottawa, Illinois, and Cape May, New Jersey. The Ottawa material occurs as a friable sandstone, which is broken down to its natural grain, washed, and screened. The grains are spherical, resembling miniature

pearls when seen under the lens. The Cape May sand is subangular and uneven in shape but larger grain sizes are obtainable, more so than with the Ottawa sand.

In Canada, sandblast sand is obtained from the decomposed rock containing friable quartz and china clay at Lac Remi, north of Montreal, Quebec; from a similar type of material near Smoky Falls, north of Lake Nipissing, 25 miles west of North Bay, Ontario; also from a friable quartzite at East Templeton, Quebec, a few miles northeast of Ottawa, Ontario. The grain of the Canadian sands is sharp. The ranges of grain size are approximately: No. 1 between 20 and 35-mesh for light work; No. 2 between 10 and 28-mesh; No. 3 between 6 and 10 and No. 4 between 4 and 8-mesh. The last two are used for the heavy cast-iron work and steelwork.

Pure, clean beach and river sands and Illinois sand are used for the preliminary or coarse surfacing of plate glass. The crushed sand is water-graded into a number of grades at the glass plants and fed to the surfacing machines. Approximately three tons of sand is required to surface one ton of plate glass.

Cutting sand, composed of sharp, solid, quartz grains, is used as the abrasive for sawing stone. It is usually ungraded and about equivalent to a No. 1 sandblasting sand.

Burnishing sand is a fine, rounded-grain silica sand of uniform size between 65 and 100-mesh, used in rolling down and burnishing gold decorations on porcelain. Tests on sandblasting sands and an interesting discussion on round versus sharp grains are given in detail in L. H. Cole's report.²⁸

Quartz

Crushed and graded quartz is used for the abrasive backing of "flint" sandpapers. Almost any deposit of massive white quartz is suitable. Being the cheapest of all the abrasive-coated paper, it still is sold in fair amount, mainly in hardware stores and by small jobbers. It is made only in the form of paper, not as cloth. True chalk flint from England and France is extensively employed for this purpose in Europe and has better cutting qualities and longer life than ordinary quartz.

Powdered quartz and silt are sometimes used for scouring compounds and for the harsher metal polishes.

Soft Siliceous Powder Abrasives

Many natural highly siliceous materials either occur as a powder or are used only in the powder form for mild abrasives. For the majority of these, use as an abrasive is of minor importance as compared with their principal applications. Among these, diatomite, pumice and tripoli are reviewed elsewhere in this volume. Their abrasive uses therefore are given only briefly here.

PUMICE

Under the name of pumice are included lump pumice and pumicite or volcanic dust, the natural powder. Lump pumice is used by manufacturers of furniture and musical instruments for dressing the wood and metal surfaces; by silver platers for preparing their metal surfaces; by lithographers for cleaning the stone surfaces; for rubbing down and polishing fine tools and instruments; by restaurants for scouring grills and cooking utensils, and for domestic and toilet uses, such as hand cleaners. Pumicite or ground pumice is mainly used as a cleanser, the thin, sharp and striated grains being particularly suitable for this purpose. It is also made up in the form of hand soaps. In 1945, a year of record production of pumice and pumicite in the United States, production exceeded the previous record tonnage of 1942 by 77 pct. Of this production, 63,704 tons valued at \$434,928, or 45 pct of the total tonnage of pumice sales, was used for cleansing and scouring compounds and for hand soaps, and about 47 pct for other abrasive uses, which include polishing compounds, polishing powders for bone, celluloid, and hard rubber, in dentists' tape and in some rubber erasers.

An artificial pumice used for abrasive purposes was made in Germany. In this process obsidian or volcanic glass preheated to 900°C is dropped down a shaft furnace against a rising draft of hot gases. The obsidian swells into porous particles and is then consolidated with lime or cement to a form resembling a pumice, which has an apparent specific gravity of less than that of natural pumice.

TRIPOLI, MICROCRYSTALLINE SILICA, AND ROTTENSTONE

The fine-grained, porous materials, tripoli, microcrystalline silica, and rottenstone, are known to the trade as "soft silicas."

Tripoli, which in the United States comes from southwest Missouri and northeast Oklahoma, is mainly used (about 70 pct of the production) in the form of made-up tripoli grease bricks or tripoli compositions for buffing and polishing. The compound is applied to a rapidly revolving belt or canvas wheel and used for the finishing or buffing of metals, plated products, and so forth. It is used also to a small extent in the manufacture of some scouring and cleaning powders and soaps; for the rubbing down of painted surfaces, such as automobile bodies. A similar but finer-grained material occurring in the northwest corner of Arkansas, about 50 miles southeast of the Missouri deposits, is used mainly for oil-well drilling mud.

Microcrystalline (sometimes erroneously termed "amorphous") silica, which comes mainly from southwestern Illinois but to some extent from Wayne County, Tennessee, also is used for buffing and polishing compounds. These compounds are termed "silica" by the trade and

are much in demand for white "coloring" operations on high-class work. Chemically precipitated amorphous silicas also are used in polishing and buffing compositions.

Both tripoli and microcrystalline silica have been mined from deposits at Harrisburg, northwestern Georgia.

Rottenstone, a fine-grained gray-buff siliceous-argillaceous limestone, comes from Antes Forte, Lycoming County, Pennsylvania, and is used as a polish base; for instance, for automobile polishes.

During 1945, in the United States, 11,113 tons valued at \$188,262, which was 61 pct of both the tonnage and the value of the total sales of these three materials, was used for abrasive purposes, mainly in grease compositions.

DIATOMITE

Approximately 98 pct of the diatomite (diatomaceous silica, kieselguhr, etc.) production in the United States comes from the deposits of California, Oregon, and Washington. The amount used for abrasives is insignificant in comparison with its other applications. As an abrasive it is mainly used in metal (silver) polishes, powders and pastes and in some automobile polishes, dental powders and pastes and occasionally as a friction agent in match heads or on the sides of boxes.

NONSILICEOUS SOFT ABRASIVES

GROUND FELDSPAR is extensively used in scouring and cleaning compounds and for a window cleaner.

CHALK (calcium carbonate) is a soft, compact, fine-grained, white limestone composed of the calcareous remains of small marine shells. A small amount of this chalk—mainly from England and France—known as "whiting" is used as a very mild abrasive for hand-polishing of nickel, gold, silver or plated ware, buttons, and similar materials.

CHINA CLAY (kaolin) and some pipe clays have been used successfully in polishing powders. Pipe clay at one time was the standard polish for naval and military tunic buttons.

BATH BRICK, used for scouring steel utensils, are made from a very fine-grained, quartzose clay found along the banks of the Parrot River in England.

MANUFACTURED OR ARTIFICIAL ABRASIVES

The discovery of the electric-furnace method for making silicon carbide, by Edward G. Acheson in 1891, began the revolution in the high-grade abrasives industry. Prior to that time, all abrasives were natural mineral and rocks, except for minor chemically prepared materials such as rouge and Vienna lime. Today, as noted before, artificial abrasives, with a few notable exceptions such as diamond and garnet, dominate if not monopolize the field of high-grade abrasives.

Artificial abrasives are essential to modern industry not only be-

cause they are superior but because they are much more uniform in quality than natural abrasives and their properties can be varied to meet differing needs of use. Modern high-speed streamlined production methods require very accurate, specialized tools with a degree of uniformity and dependability that cannot be met with natural abrasives.

While detailed studies of these materials cannot be given here, brief summaries are included because they compete with and supplant natural abrasives, and because, in most cases, they are products made from mineral raw materials.

TABLE 5—*Crude Artificial Abrasives Sold, Shipped or Used from Manufacturing Plants in the United States and Canada*

Year	Silicon Carbide ^a		Aluminum Oxide ^a		Metallic Abrasives ^b		Total	
	Short Tons	Value	Short Tons	Value	Short Tons	Value	Short Tons	Value
1936	29,342	\$2,139,919	69,825	\$3,913,155	24,667	\$1,221,912	123,834	\$7,274,986
1937	30,365	2,215,318	86,401	4,749,497	28,031	1,399,772	144,797	8,364,587
1938	25,346	1,904,925	53,220	3,098,132	25,771	1,234,977	104,337	6,238,034
1939	24,206	1,713,207	50,468	3,047,337	42,015	1,743,859	116,689	6,504,403
1940	33,042	2,359,876	98,531	5,464,986	50,016	2,317,829	181,589	10,142,691
1941	44,962	3,325,928	147,759	9,067,732	86,309	4,050,659	279,030	16,444,319
1942	61,681	4,904,309	183,633	12,719,337	106,442	5,618,913	351,756	23,242,559
1943	69,706	5,912,590	217,425	13,202,270	124,954	7,083,141	412,085	26,198,001
1944	56,291	4,717,675	185,573	11,668,838	144,540	8,441,505	386,404	24,828,018
1945	53,773	4,238,655	147,016	9,130,093	146,771	8,524,073	347,560	21,892,821
1946	63,849	5,457,903	132,084	8,367,158	111,512	6,387,819	307,445	20,212,880
1947	63,724	5,633,811	160,022	10,158,432	149,697	12,060,215	373,353	27,852,458

^a Bureau of Mines not at liberty to publish data for United States separately; figures include material used for refractories and other nonabrasive purposes. In 1945, silicon carbide consumed in refractory and other nonabrasive uses was about 44 pct of total production and aluminum oxide was about 4 pct. Production of silicon carbide in 1945 was nearly 75 pct of capacity; of aluminum oxide 63 pct of capacity; and of metallic abrasives about 70 pct.

^b Figures include only shipments from plants in the United States and cover only steel shot and grit.

Manufactured abrasives may be divided into three main groups: (1) electric-furnace products, (2) chemical precipitates; with (3) several miscellaneous additions.

The production of certain types of artificial abrasives for recent years is shown in Table 5, taken from Bureau of Mines Minerals Yearbooks for 1940 and 1947.

Electric-furnace Abrasives

Electric-furnace abrasives include silicon carbide, aluminum oxide and boron carbide. Tungsten carbide, tantalum and titanium carbides

are used in making cemented-carbide high-speed cutting tools but are not considered as abrasives in customary usage.

SILICON CARBIDE

Silicon carbide, with the chemical formula SiC , is commonly known by the trade names Carborundum, Crystolon, Carbolon, and others. It is made by fusing a mixture of high-grade silica sand and carbon in an electric furnace. The preferable form of carbon used today is petroleum coke, but anthracite and coke made from coal low in ash have been used. High iron and alumina in the ash are objectionable in that they tend to assist in the formation of elemental graphite and metallic silicon during the reaction. High-ash carbons make impure grades of silicon carbides.

"Silicon carbide (p. 2 of ref. 38) is made by charging a resistance type electric furnace with pure glass sand . . . , finely ground petroleum coke, sawdust and common salt. The silicon of the sand combines with the coke, which is carbon, to form silicon carbide. The sawdust makes the mixture porous so that the carbon monoxide gas formed in the course of the chemical reaction can escape freely." The salt (sodium chloride) combines with the various impurities in the sand and coke to form chlorides, which can then be eliminated from the mix, by volatilization. The temperature at the core of the furnace is about 2200°C . If the temperature is too high, silicon carbide decomposes, the silica being volatilized and the carbon becoming graphitized. The time of a run is about 60 hr (36 hr heating and 24 hr cooling). At the end of the run the core consists of loosely knitted silicon carbide crystals surrounded by unreacted or partially reacted raw materials. The quality of the product depends largely on the raw materials used and the accuracy of control and operation of the furnace.

Several types of product are made in which the hardness and toughness of the grains are varied. A special surface treatment is given to grains for coated abrasives to increase adhesion of the glue.

The lump material from the furnace is crushed, first in jaw crushers then in rolls, passed through a magnetic separator to remove magnetic impurities, and then washed to remove dust. The grains are then dried and screened mechanically into 20 or more standard sizes, from 8 to 240-mesh. The finer flour sizes are made by water flotation and sedimentation.

FUSED ALUMINUM OXIDE

Aluminum oxide abrasives are made in electric-arc furnaces. Bauxite, the crude raw material, should be low in silica (less than 2.5 to 3 pct), but the iron content is not critical. The ore as mined is crushed, then calcined in rotary kilns to remove both free and combined water. The calcined ore is mixed with iron borings (about 2 pct) and

ground coke (about 3 pct) and charged into the furnace. The coke reduces the impurities, which combine with the iron and sink to the bottom of the furnace.

At the end of the melting period, the charge is allowed to cool under controlled conditions, to obtain desired texture. The finished, crystallized alumina consists of about 95 pct Al_2O_3 , 3 pct TiO_2 , 1.5 pct SiO_2 and 0.5 pct Fe_2O_3 . For certain purposes pure alumina is used instead of calcined bauxite, making a product with about 99 pct Al_2O_3 .

Fused alumina ordinarily is very tough but for some uses a weaker grain structure is needed. This may be produced in several ways. It may be done: (1) by decreasing the size of the crystal, either by rapid cooling or by adding small amounts of certain chemicals to the charge, (2) adding to the charge an alkali that gives off a gas as the molten mass is solidifying. This gas causes perforations in the crystals, which weaken the structure.

The cooled mass from the furnace is crushed, screened and cleaned in about the way that silicon carbide is treated. Here also several types of grain are made, varying in toughness, type of fracture, glue adhesion, and other properties.

USE OF ARTIFICIAL ABRASIVE GRAINS

The finished abrasive grains may be sold as grains, to be used* for a wide variety of grinding, drilling, rubbing, lapping and polishing purposes, such as grinding plate glass and sandblasting. They may be glued or cemented to paper or cloth to make such coated abrasives as sandpaper and emery cloth, or to felt, wood, leather, canvas or other materials to make a great variety of grinding, polishing and buffing belts, wheels, disks and other shapes. They may be bonded with grease or glue to form bricks and sticks used for buffing and polishing. They may be bonded with rubber, sodium silicate, shellac, artificial resin, or ceramic binders and shaped into grinding wheels, pulpstones, hand sharpening and honing stones, rubbing stones, nonslip abrasives, tile, and so forth (see also page 6).

Nonabrasive uses for these manufactured grains include a very wide range of refractory and chemical applications, from refractory brick to kiln muffles and chemical laboratory ware.

BORON CARBIDE

Boron carbide is a relatively new artificial abrasive introduced in 1934 by the Norton Company under the name of Norbide. Its chemical formula is B_4C . It is the hardest artificial abrasive known to man but it is far from the hardness of the diamond (see Table 1). It is made from boric oxide, B_2O_3 , and carbon in the form of petroleum coke, in

a carbon resistance furnace at a temperature of about 2600°C. The finished product is crushed and ground to make a range of sizes of grains and powders. In grain form it is used for grinding and lapping operations for jobs previously possible only with diamond dust. Pulverized Norbide may be molded under very high heat and pressure to form extremely wear-resistant products such as sandblast-nozzle liners, thread guides, extrusion dies, and all types of extremely accurate plug, snap, and ring gauges. It is not manufactured into bonded wheels or sharpening stones.

Metallic Abrasives

Metallic abrasives include crushed steel, steel shot, angular steel grit, steel wool, brass wool and copper wool. The following description of the first three of these products is by Johnson and Schauble:³⁴

"Crushed steel is made from high-carbon and crucible sheet steel specially treated to impart brittleness. It is then crushed to sizes ranging from 2 to 200-mesh. After screening, each batch is heat-treated and separated into 25 sizes ranging from 20 to 200-mesh. Sizes from 70-mesh upward are screened on silk bolting cloth, and the finer sizes in powder form are used in steel cement, various chemical compounds, and fire-works sparklers.

"Steel shot is merely chilled cast iron. Only raw materials of the highest grade, including selected scrap and charcoal iron, are used in its manufacture; these are melted in a cupola. During the casting period, the molten metal is separated into small spherical globules by directing high-pressure steam or heated compressed air against the stream of metal. The globules are blown into water and cooled. The shot, made brittle by the rapid cooling, is heat-treated to impart a temper of hardness and graded by mechanical means into 15 sizes that range from 4 to 90-mesh. Coarse material left on the 4-mesh screen is granulated by specially designed crushing equipment and in this form is known as angular steel grit. The crushed material is heat-treated to impart toughness and durability, then graded into 15 sizes ranging from 7 to 100-mesh. Steel shot and angular steel grit are used for many abrasive purposes."

Steel wool, made from both ordinary and stainless steel, in various finenesses, is used for finishing wood and soft metals such as aluminum, and for scouring and cleaning. It is made, in several types of machines, by shaving or scraping continuously moving wire with a fixed serrated cutting tool. Brass and copper wool are used chiefly for household cleaning.

Chemical Precipitates

Chemical precipitates, mainly oxides, all have a very fine grain size and are used as final polishing agents.

IRON OXIDES

ROUGE, a ferric oxide, has its largest use in the polishing of plate glass, but is also widely used in powder, paste, coated cloth and stick form for polishing precious metals, stone, and other materials to give a final high luster.

CROCUS, similar to rouge in composition but a purplish red in color, is used in finishing cutlery and some brass work.

BLACK ROUGE, a precipitated black magnetic iron oxide, is used primarily in plate printing inks and in paints, but has small abrasive application.

OTHER PRECIPITATES

CHROMIUM OXIDE, or "GREEN ROUGE," is used chiefly for platinum and stainless steels.

TIN OXIDE is used largely for polishing glass and precious stones.

PUTTY POWDER is a mixture of tin oxide and oxalic acid, used for about the same purposes as tin oxide.

CERIUM OXIDE is a relatively new polishing agent, which came into use during World War II for polishing glass and as a substitute for tin oxide for some other uses.

MANGANESE DIOXIDE is reported as having limited abrasive use.

MAGNESIA in the soft precipitated form has been noted as a mild polishing powder. The hard-burned variety, artificial periclase, has been used also as an abrasive.

CALCIUM CARBONATE, precipitated, is a mild abrasive used in some dentifrices.

CALCIUM OXIDE or LIME, under the names of Vienna lime or Sheffield lime, has important abrasive uses. This so-called Vienna lime (originally from Vienna, Austria), which is used on the American continent in grease-brick buffing composition, is obtained from certain beds of dolomite at Francis Creek and Manitowoc, Wisconsin. Vienna lime is made by calcining the dolomite and cleaning and grinding to a certain fineness. It is packed in carefully sealed containers. As soon as the lime becomes hydrated it ceases to function and also attacks the grease compositions. It is used for the buffing of brass, copper, bronze, steel, pearl, celluloid, and similar materials but its main use is for the "coloring" of nickel after plating, as it gives it a deep "under-surface" blue peculiar to the metal. Lime attacks aluminum, therefore it is not used on that metal.

The use of porcelain blocks and pebbles for grinding mills has been noted. This "porcelain" may consist largely of zirconium oxide or silicate, or of mullite converted from andalusite, kyanite or dumortierite.

Miscellaneous Manufactured Abrasives

GLASS, crushed and screened, has been used for coated abrasives to make "glass" paper.

LAMPBLACK, known as "SATIN ROUGE," finds some use for polishing celluloid and bone.

CLAY, very hard burned and finely pulverized, has been reported as used as an abrasive for polishing metal.

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CHAPTER 2

ASBESTOS

BY G. F. JENKINS*

ASBESTOS is a general term embracing the fibrous varieties of a number of minerals. Of these, the hydrous magnesium silicate, chrysotile ($\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9$), a variety of serpentine, is the most abundant and useful to industry.

All other types of asbestos belong to the amphibole group of minerals and are classified as: crocidolite, $\text{NaFe}(\text{SiO}_3)_2 \text{FeSiO}_3$; anthophyllite, $(\text{MgFe})\text{SiO}_3$; amosite, also a ferromagnesium silicate but with iron content higher than that of anthophyllite; tremolite, $\text{CaMg}_3(\text{SiO}_3)_4$; and, actinolite, $\text{Ca}(\text{MgFe})_3(\text{SiO}_3)_4$.

PROPERTIES

The commercial value of asbestos depends largely on the physical property that permits it to be readily separated into fine filaments of high tensile strength and flexibility, which, coupled with the fact that it has the quality of incombustibility of a mineral—in distinction to vegetable and animal fibers—makes it of unique usefulness for many purposes. To some extent, the value depends upon the length of the fiber, although extreme length is neither necessary nor desirable for most purposes.

Chrysotile occurs as cross-fiber veins, in which the asbestos fibers are approximately at right angles to the vein walls, with vein width—or fiber length—seldom exceeding 2 or 3 in.; also as slip-fiber, in which the fibers lie in the same plane as the vein or on slippage planes. A cleanly broken vein of cross-fiber has a pearly luster and may range from a deep green or brown color to light shades of yellowish green or cream. When of good quality, the fiber filaments forming the vein may be easily drawn away from their neighbors and exhibit a fine silkiness and pure white color. They may be twisted into a thread and when flexed between thumb and fingers are found to be strong and pliable. Chrysotile withstands comparatively high temperatures without breaking down completely or fusing but begins to lose water of crystalliza-

* General Manager, Asbestos Corporation Ltd., Thetford Mines, Quebec.

The author wishes to acknowledge the help and advice given him by A. L. Penhale, President, Asbestos Corporation Ltd., also the assistance of I. C. Campbell, P. E. Breton and M. K. Senicie, of the same company.

tion at about 450°C and becomes brittle. It is readily attacked by acids. Fibers of highest quality generally contain more than 13 pct water of crystallization.

Slip-fiber chrysotile may be equally strong and flexible but is unsuitable for spinning, although useful for other purposes.

Crocidolite has a characteristic deep dusty blue color in the fiberized as well as in the crude state. This variety is less resistant to heat than chrysotile, fusing at a comparatively low temperature. On the other hand, it withstands the effects of acids and alkalis much better and is said to have a higher dielectric strength. Its spinnability is inferior to that of chrysotile.

Amosite usually is of a yellowish gray shade. The fibers, while having good tensile strength and greater average length than chrysotile or crocidolite, are relatively harsh and do not spin well. Its resistance to acids and alkalis is fairly high, though lower than that of crocidolite. It is superior to crocidolite in withstanding heat.

Of the three remaining fibrous amphibole minerals, actinolite, tremolite, and anthophyllite, the two last named, because of their resistance to attack by acids, are especially suitable for use in filtration. The fibers lack tensile strength and those of anthophyllite, in particular, are brittle.

DISTRIBUTION OF DEPOSITS

United States

Asbestos deposits in the United States are very limited in extent and distribution. The largest known reserves are in northern Vermont, where the asbestos-bearing serpentine zone of Quebec extends into that state. The developed ore is chrysotile, almost entirely of the slip-fiber type. It is reported, however, that diamond drilling has recently revealed cross-fiber of good quality in the same zone as that of the slip-fiber ore body being currently mined.

In Arizona, chrysotile occurs in veins following the bedding of serpentized dolomites near diabase intrusions. The fiber is of high quality and is particularly suitable for insulation of electrical equipment because of its low iron content; unfortunately, however, it cannot be considered a potentially important reserve.

Some cross-fiber chrysotile occurs also in Montana and California but of insufficient grade or extent to have been actively developed to date.

Anthophyllite is mined in Georgia and North Carolina. Further occurrences of this mineral and other varieties of amphibole asbestos have been found in the southern Appalachian Mountains, also in California, Oregon, Washington, Idaho, and Alaska.

Canada

By far the most important asbestos deposits of the North American Continent are in the southern part of the Province of Quebec, Canada, in the area known as the Eastern Townships. Here, chrysotile of good quality has been produced for nearly three quarters of a century and there are known and indicated reserves sufficient for many more years at the present rate of exhaustion. There are two main deposits, one near Danville and the second some 40 miles to the northeast in the Thetford mines, Black Lake, area. On the fringes of these main centers are producing mines at Nicolet, near Danville, and at East Broughton, a further 20 miles northeast of Thetford mines.

Elsewhere in Canada, notably in northern Ontario and northern Quebec, occurrences of chrysotile asbestos have been found, although, to date, no deposits of commercial importance have been developed.

Russia

Russia possesses chrysotile deposits of considerable size and economic importance. Previous to the war, the locality being most actively exploited was at Asbest, in the district of Bajenova (Bazhenova) on the eastern slope of the Urals, where reserves were reported as being very extensive. Other large asbestos-bearing serpentine areas are north of the Asbest district. In 1938, production was second only to that of Canada. Since that year, however, no statistics have been available.

Africa

Africa ranks third in the importance of known deposits. In addition to its large reserves of chrysotile, it has the distinction of being the only important producer of crocidolite and the sole producer of amosite. Chrysotile is mined in substantial tonnages in the Shabani district of Southern Rhodesia and in recent years the Havelock area, which is in Swaziland near the Transvaal border, has become an important source of supply. The more accessible deposits of the Barberton and the Carolina districts of the Transvaal have apparently been largely depleted.

Crocidolite, "Cape Blue," is actively exploited in the Union of South Africa's Cape Province, in an extensive belt in the Kuruman district that continues into the districts of Vryburg and Mafeking, this variety being the only asbestos mined in the province. Crocidolite also occurs and is mined from numerous small workings in the Pietersburg district of northeastern Transvaal.

Amosite also is found in the Pietersburg district, where in some places it is quite closely associated with the crocidolite; it occurs alone in the neighboring district of Lydenburg. These are the world's only known sources of amosite.

Kenya and Uganda have been reported as minor producers of asbestos, presumably the anthophyllite variety of amphibole only.

China

The possible asbestos ore reserves of China may be substantial. Very little information is available except that production figures have risen since 1939 to around 20,000 tons annually. The location of the mines from which this increased production is derived has not been reported. It is known, however, that small-scale mining operations have been carried on for many years in the Laiyuan district of Hopei, where chrysotile occurs in altered limestone near the contact with an intrusive granite. Chrysotile asbestos is known to occur also in several other provinces. The problem of transportation has been a handicap to more active development.

Italy

Northern Italy, the cradle of the asbestos industry, continues to produce an important tonnage of fiber. This country has been almost the sole supplier of a good grade of tremolite asbestos, some of which has been of sufficiently high quality to have been used for spinning in the past. This fiber is mined in the vicinity of Turin in the Lanzo, Susa and Aosta valleys as well as near Sondrio, east of Lake Como. Slip-fiber chrysotile, also, is mined in the Lanzo valley, where it is recovered from a highly sheared serpentine similar to that worked at East Broughton in Canada.

France

France has continued to produce a small tonnage from a chrysotile deposit in the western Alps, and in Corsica has deposits of short-fibered chrysotile, in which there is revived interest due to the world shortage of asbestos.

Minor Production

A small production has been obtained from French Morocco and also from Egypt. Turkey has produced slightly more on the average, and is reported to have a potential source of supply in the Province of Kara in Turkish Armenia.

The production of Finland, which is several thousand tons of fiber yearly, is derived from the eastern part of the country and consists of anthophyllite.

Cyprus probably still has moderately large reserves of short-fibered chrysotile. Asbestos has been mined on the island, it is believed, since the ancient Greeks and Romans made use of long-fiber amphibole for lampwicks and cremation sheets. Amphibole deposits still exist, although modern production is entirely from the serpentine areas.

Several South American countries produce asbestos fibers in minor

quantities. In Venezuela a small plant has been constructed to exploit the chrysotile occurring in serpentinized basic rocks west of Tinaquillo. Some asbestos is also mined in Brazil. In Bolivia there is an occurrence of crocidolite from which a small production has been derived.

In Western Australia crocidolite deposits, similar in origin to those of South Africa, are in process of development in the Hamersley Range. Some production of chrysotile and anthophyllite has been reported from Western Australia, together with chrysotile from New South Wales, South Australia and Tasmania. Occurrences of the latter variety have also been recorded in Victoria and Queensland, although apparently not in commercial concentrations.

In New Zealand there has been some revived interest in the chrysotile deposits of the Flora district, Northwest Nelson.

India and Indochina produce a few hundred tons of asbestos annually. The potential reserves are doubtful, but in the Addapah district of Madras Presidency small quantities of a very fine grade of chrysotile have been mined from a narrow band occurring in dolomitic limestone, close to the contact of a dolerite sill.

The asbestos reserves of Japan apparently are quite limited. Stimulated by requirements during the war, production rose to nine thousand odd tons in 1944. The locale of production is not known. Deposits are known to exist, however, in the island of Kyushu near Nagasaki and Kumamoto and there are occurrences in Korea. The mines at Chinchow, Manchuria, were worked by a Japanese company for many years.

Asbestos occurs in a number of places in Newfoundland. In the Lewis Hills area near Port-au-Port, where good quality chrysotile has been known to exist for many years, work has been done recently but nothing of commercial importance has been developed.

POLITICAL AND COMMERCIAL CONTROL

From the foregoing, it is apparent that all the known major asbestos deposits, except those of Russia, are in countries of the British Empire. English capital controls the majority of Rhodesian and South African mines, also one important property in Canada. Several of the Canadian properties, including the largest single producer, are controlled by United States companies while Canadian capital has controlling interest in others. Russian mines, of course, are exclusively state-owned.

PRODUCTION AND CONSUMPTION

The demand for asbestos in recent years has greatly exceeded supply. This situation is world-wide and few, if any, industrial nations have been able to procure sufficient fiber to satisfy the requirements of manufacturers using asbestos in their products. Production of the

raw material by the mines, particularly in Canada, has increased steadily over the past three years and is continuing to increase. Much of the added output has been in the shorter grades, however, and has not been of much real assistance to the manufacturer of asbestos cement products using so-called shingle-fiber grades.

Countries in which manufacturing had been curtailed during the war years are again in the market. In the meantime, the consumption of asbestos in the United States, where peak figures were reached in the period from 1941 to 1943, has continued to increase, so that in 1946 the amount used was nearly double the 1938-1940 average and was still greater in 1947. Previous to World War II, the United States consumed about one half of the world's production.

In 1946 Canadian mines accounted for over half a million tons of the raw product, representing about 77 pct of the world's total from all sources outside of Russia.* When statistics for 1947 are complete, undoubtedly they will show this figure to have risen to approximately 80 pct. Of this, 83 pct by weight in 1946 was exported to the United States, which constituted over 94 pct of the asbestos imported by this country in that year. Domestic sources supplied the United States with less than 3 pct of its total requirements.

Statistics indicate that Africa, the only other major producer aside from Russia, had 14.9 pct of the world's total in 1946 (Russia again excluded) comprised of 8.3 pct from Rhodesia, 3.7 pct from Swaziland and 2.9 pct from the Union of South Africa.

The accompanying graphs (Figs 1 and 2) show asbestos production from Canada, Rhodesia and the Union of South Africa for the years 1936 to 1947 in short tons and Canadian dollars respectively.

Canada consumes a very small but growing percentage of its production. The other principal consuming countries, aside from the United States, are: Great Britain, Russia, Belgium, France, Italy, South American countries collectively, Australia and Mexico. Consumption in the three last named has expanded considerably in recent years. Germany and Japan, which were large users of asbestos before the war, have received little or no asbestos in recent years.

PROSPECTING AND EVALUATION

Chrysotile asbestos, as described earlier, is a form of serpentine and occurs in association with this mineral. All of the extensive and more important deposits of this variety are found in large bodies of serpentinized olivine-rich ultrabasic igneous rocks, such as dunite and peridotite. Outcrops of these rocks usually are recognizable by the yellowish or reddish brown appearance of their weathered surface, although

* The latest figures on production of asbestos in Russia is 86,000 metric tons in 1938. This represented 19 pct of the world's total at that time.

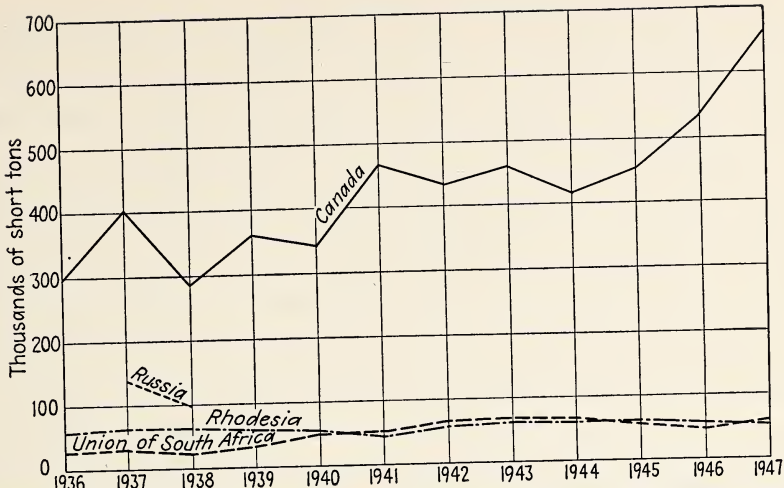


FIG 1—PRODUCTION OF ASBESTOS IN CANADA, RHODESIA, RUSSIA, AND UNION OF SOUTH AFRICA.

Canadian figures do not include sand and gravel. South Africa figures include Swaziland from 1939.

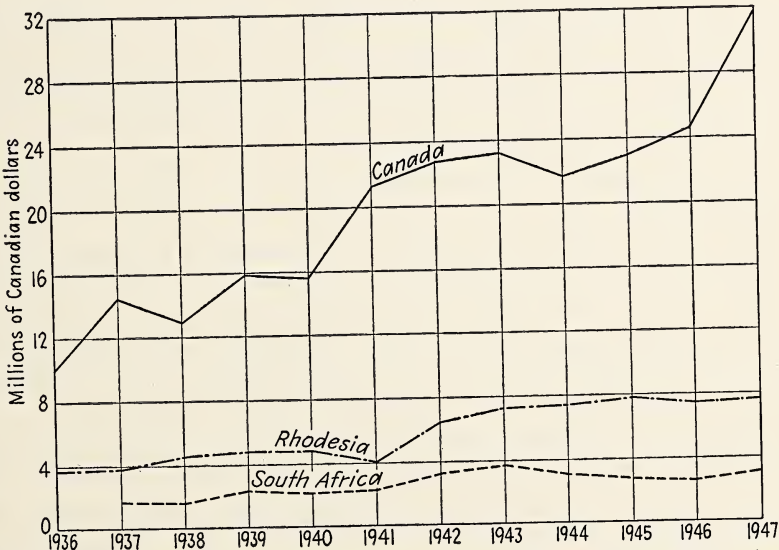


FIG 2—VALUE OF ASBESTOS PRODUCTION IN CANADA, RHODESIA, AND SOUTH AFRICA.

South African figures based on domestic and export sales.

Rhodesia: figure of \$4.33 per pound used for conversion of pounds sterling to Canadian dollars.

where less weathered or of lower iron content, the color may be greenish or of lighter shades. Associated rocks generally found intruding the serpentinized ultrabasics are granite or other acidic phases such as aplite, alaskite, or feldspar porphyry in the form of dikes or sills. High-grade deposits often are found quite close to these intrusives.

Chrysotile is found in serpentinized dolomitic limestone, as in Arizona, where the association is with diabase sills, and the veins, instead of being disseminated throughout great masses of the rock, generally occur in relatively narrow bands following the bedding. Another type of occurrence in dolomite is that where the veins are arranged concentrically in a band of serpentine surrounding a spheroidal core of serpentine, much as the shell of an egg. This type is of very limited economic importance but is of academic interest at least. Examples of the spheroid type are common in the Grenville limestone east of Ottawa, Canada, and in the Flora district, northwest Nelson, New Zealand. A somewhat similar occurrence, also to be found in the last named district and in the Lewis Hills of Newfoundland, is where asbestos veins form a peripheral zone surrounding lenses of gabbro or boulder-shaped differentiates in serpentinized peridotite.

Crocidolite, the blue variety of asbestos as found mainly in Cape Province and the Transvaal, South Africa, occurs as cross-fiber veins in highly folded banded ironstone, which may be described as a ferruginous quartzite. The productive horizons are mainly in the lower part of the ironstone series not far from underlying dolomite or lying close to thin sheets of intrusive dolerite.

Amosite asbestos is found closely associated with the crocidolite in the Transvaal.

Asbestos is resistant to weathering, so that where a deposit outcrops the prospector has little difficulty in recognizing it, and may make a fairly accurate evaluation of the exposed portion by visual inspection. Serpentine is particularly stable chemically and, although relatively soft, is likely therefore to be found forming the intermediate features of topography such as low knolls or less rugged hills.

In addition to a knowledge of the actual host rock of asbestos, those exploring for new deposits would be well advised to direct their attention to the rocks commonly found associated with existing commercial deposits, as, for instance, the granites and aplites, such as those of the Thetford district of Canada or the Shabani district in Rhodesia.

Asbestos fiber that has been removed from its host rock by natural processes of weathering and erosion may be found intermixed in clay or other overburden, or in the talus of a steep hillside, and thus assist in the discovery of a deposit. Boulders in which the asbestos veins are still intact may be traced in stream beds and serve to guide the searcher.

In some cases the use of magnetometer observations may be of assistance in exploration for asbestos, but this method has been little used. Where the initial examination of outcrops indicated favorable conditions, further exploration is generally conducted by conventional methods of stripping, trenching, diamond drilling and test pits.

In diamond drilling, the larger diameter cores are favored for better recovery. Normally, however, the diameter need not be larger than the $1\frac{1}{8}$ in. Good core recovery is difficult where intense shearing is encountered but the better grade portions of a deposit, where the more valuable cross-fiber veins are found, are generally sufficiently solid for good recovery. The usual practice is to evaluate the diamond-drill cores visually. A reasonably accurate estimate of the percentage of fiber content can be made mathematically by taking the sum of vein widths over measured lengths of core. In addition to this, the unit value of the fiber itself per ton will depend on its quality and length. It is necessary therefore to assess the quality and grade and arrive at an estimated value of the average grade that would be expected to be recovered. The latter value, in terms of per ton of fiber, multiplied by the percentage content will give the value per ton of ore.

An engineer making an evaluation would normally have at least part of the core treated in a laboratory equipped to separate fiber from the rock, and would determine the grade of the fiber by standard testing methods for asbestos. The results thus obtained can be used as a guide but care must be taken to make due allowance for the general attitude of the veins intersected: a section of core containing a vein running lengthwise could obviously give very misleading results.

For more accurate evaluation it is necessary to take large representative bulk samples and have these treated in a commercial asbestos mill or pilot plant.

MINING METHODS

To date, by far the greatest proportion of asbestos ore has been extracted by opencast mining methods. Obviously, however, some deposits are worked more economically by underground systems even in the initial stages. Some of the older mines, where open-pit operations have been continuous for many years, are now changing over to underground systems as greater depths are reached.

Several of the larger Canadian mines are classic examples of the varied methods used; having progressed stage by stage from simple open quarries with boom or overhead cableway derricks, where boxes or skips were loaded by hand, to mechanized loading on a larger scale by power shovels into cars or trucks, with equipment ranging up to 6-yd and 8-yd shovels and standard-gauge railway cars, although the largest equipment mentioned is the exception rather than the rule.

Other means have been, and are being, used to suit special condi-

tions. Glory-hole mining has been quite successfully employed in Canada although better suited for milder climates where snow and ice do not block the draw points in winter operations. Shrinkage and sub-level stoping systems have been discarded for more economical methods in mining some of the larger ore bodies, although satisfactory in particular cases. Deposits such as the flat-lying beds of Arizona, which outcrop on steep canyon sides, must be worked from adits with extraction by room-and-pillar or longwall methods.

In some of the larger Canadian deposits where open-pit mining has been pursued to the economic limit, a system of block caving has been very successful. By this method development is carried to a considerable depth below the surface and large blocks of ore are extracted with a minimum of drilling and blasting, by undercutting and allowing the ore to cave and crush from its own weight. Space does not permit a detailed description but the accompanying drawing (Fig 3) shows the development of a typical block with grizzly drifts and raises, through which the broken ore is drawn into chute raises and thus into cars that are hauled to a shaft. As caving proceeds it breaks through eventually to the surface and then, as the plug of broken ore descends, backfill of mill tailings is brought in by conveyor and the hole is kept filled to minimize subsidence of the walls (Fig 4). No pillars are left between blocks but the practice is to allow the backfill of a worked-out block to consolidate before caving is started in an adjacent one.

At one mine, which is currently being prepared for block caving, the grizzlies are being supplanted by scam drifts and raises for use with scrapers.

In asbestos mining, steel and concrete are generally used instead of timber where support of the workings is required, and all forms of wood are kept out of the mine as far as possible, the reason for this being that wood splinters are difficult to separate from asbestos fiber when once admixed with the rock. Better practice, therefore, is to keep it out.

PREPARATION FOR MARKET

In the early days of the asbestos-mining industry, production was mainly by hand methods, in which the veins of longer fiber only were selected and cobbled to remove adhering gangue. The grades thus prepared for market were called crudes and, in fact, the designation is still used for the small proportion that continues to be produced in this way. As uses developed for other than the longest fibers, mills were built in which the ore was crushed to free the smaller veins from the enclosing rock, and the fiber was separated by screening and other means. As markets continued to expand and new uses were progressively found for shorter grades of fiber, mills grew in size, so that at present there are a number with capacities of from 2000 to 4000 tons per day, and

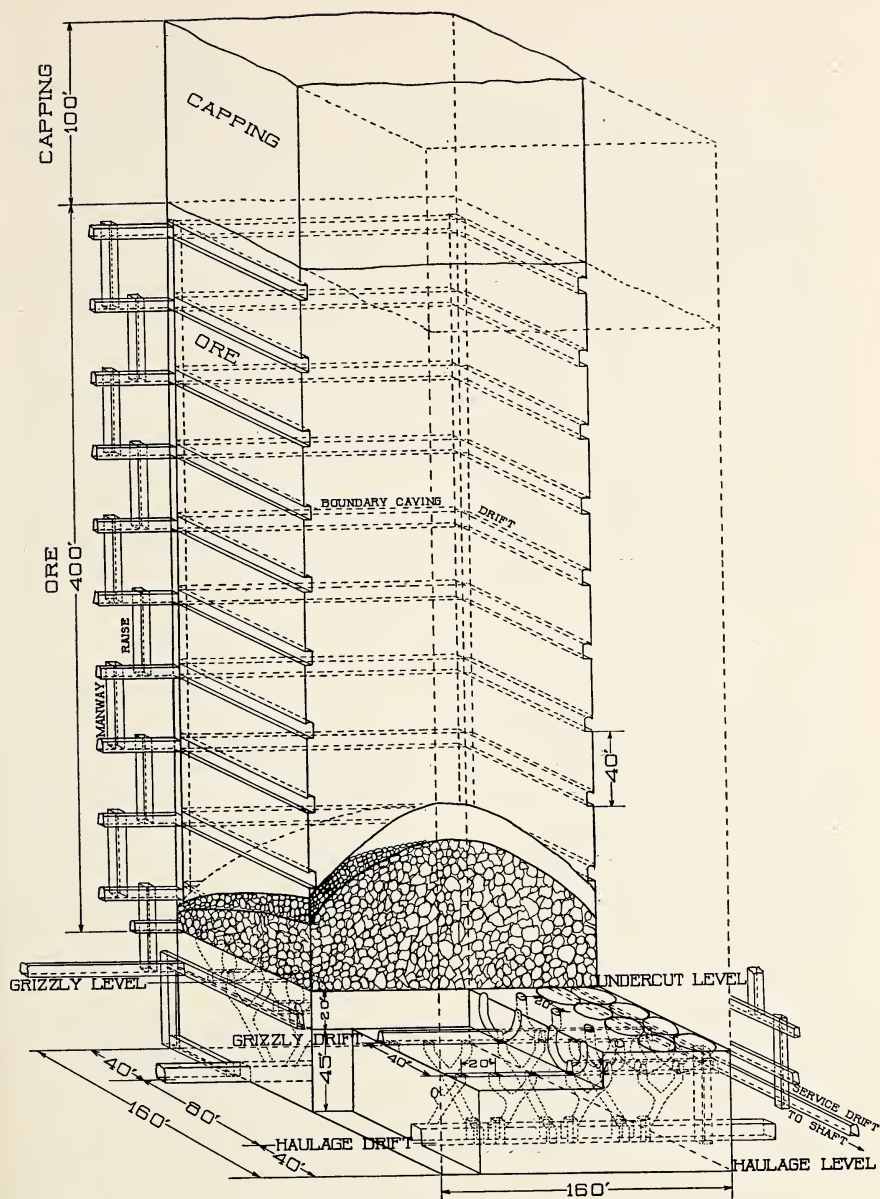


FIG 3—DEVELOPMENT OF A TYPICAL BLOCK OF ASBESTOS FOR CAVING.

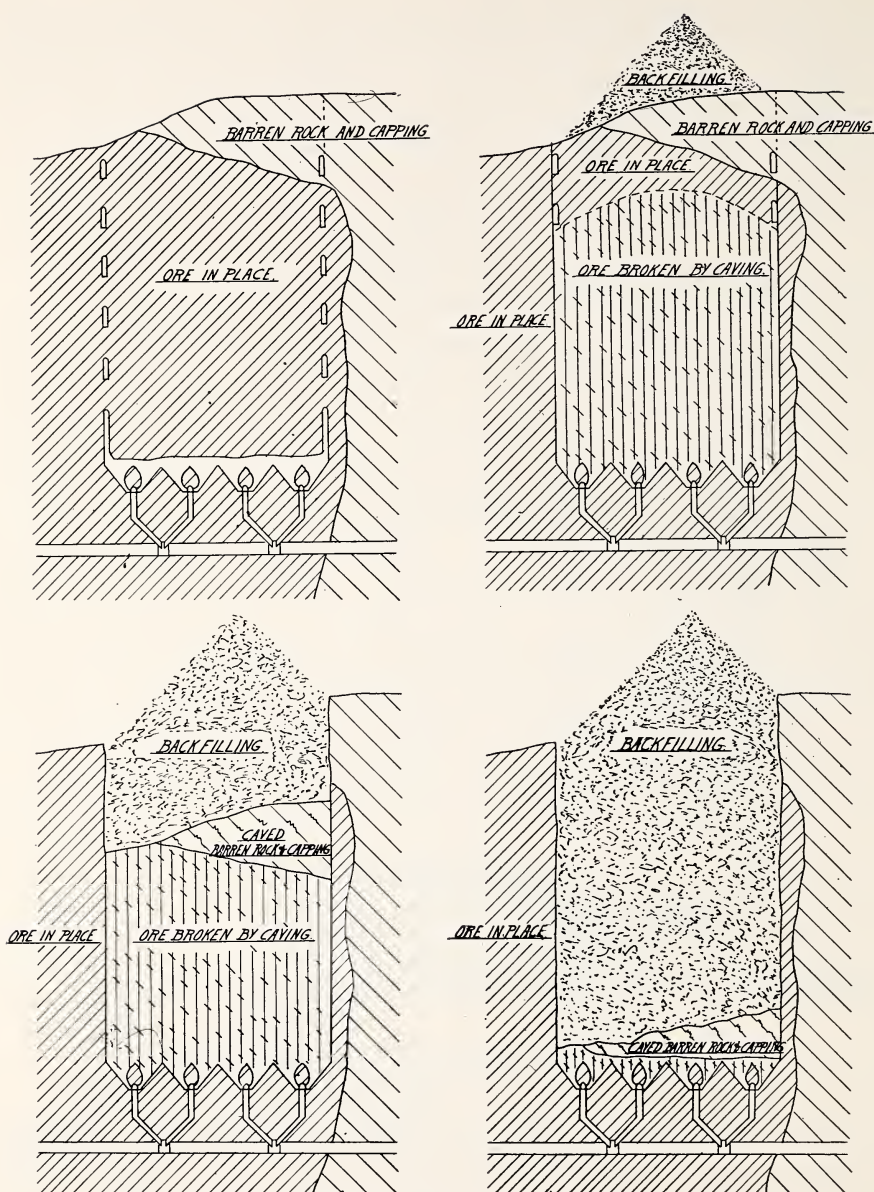


FIG 4—PROGRESSIVE STAGES OF BLOCK CAVING IN MINING ASBESTOS.

one operation has a single mill capable of treating 10,000 tons of ore daily.

Asbestos fibers are strong and tough, and can be separated comparatively easily from the rock or gangue by a crushing action, which causes the more brittle material to shatter and leave the fibers free. Their removal from the accompanying barren material can then be

effected by currents of air or water. All existing mills operate on a dry process in which the separation is largely by air suction. The usual application of this principle is by means of hoods, in effect very much like oversized vacuum cleaners, installed over the lower end of shaking screens: the screen removes fine sand and dust and the suction lifts the fiber away from the crushed rock.

While, as stated, asbestos fiber is strong and tough, the action of crushing and, to a greater extent, grinding, does to some degree cut and otherwise damage the filaments. For this reason it is the aim of operators to select milling equipment that will effect the necessary reduction with the least amount of abrasive action, within the economic limits for the particular ore being treated. The trend in asbestos milling is toward the use of machines giving more positive particle-size reduction by straight crushing action in the primary and secondary stages of milling, and moving the fiberizers—the machines that fluff or “open” the small bundles of fibers—farther along in the flow where mainly the very short grades only, and those more difficult to “open,” are affected. Because of this, fewer hammer crushers, cyclone mills and disintegrators are being used, and more of the work is done with cone crushers or other types of modified gyratories. One comparatively recent installation in South Africa employs pan crushers, which work on the principle of a chaser, with good results. At one time rolls were in great favor because of their almost ideal action in releasing fiber with minimum damage. Low capacity and high maintenance cost, however, has relegated these machines to a minor role, such as the preparation of some grades of crude.

In the accompanying flowsheet (Fig 5), an attempt has been made to give a generalized representation of present Canadian milling practice in a somewhat simplified and abbreviated form.

Milling Machines

No detailed description of the equipment used in asbestos milling will be given herein but it may be of interest to note certain features and to describe briefly some of the machines peculiar to the industry.

Primary jaw crushers are generally 36 by 42 in. in size but some operations are using 48 by 60-in. machines requiring 200 to 250 hp and with a capacity of 250 tons per hour on average ore. For the most part, they are of standard design, although it is preferable to have a smaller angle of nip than usually is possible with a standard frame and, at the same time, retain full size of opening. It is considered that the nip angle should be 21° to 23° . Most manufacturers of jaw crushers build machines with a special deep frame to attain this smaller angle between the fixed and the swinging jaw. The desirability of this feature arises from the fact that often there is a tendency for pieces

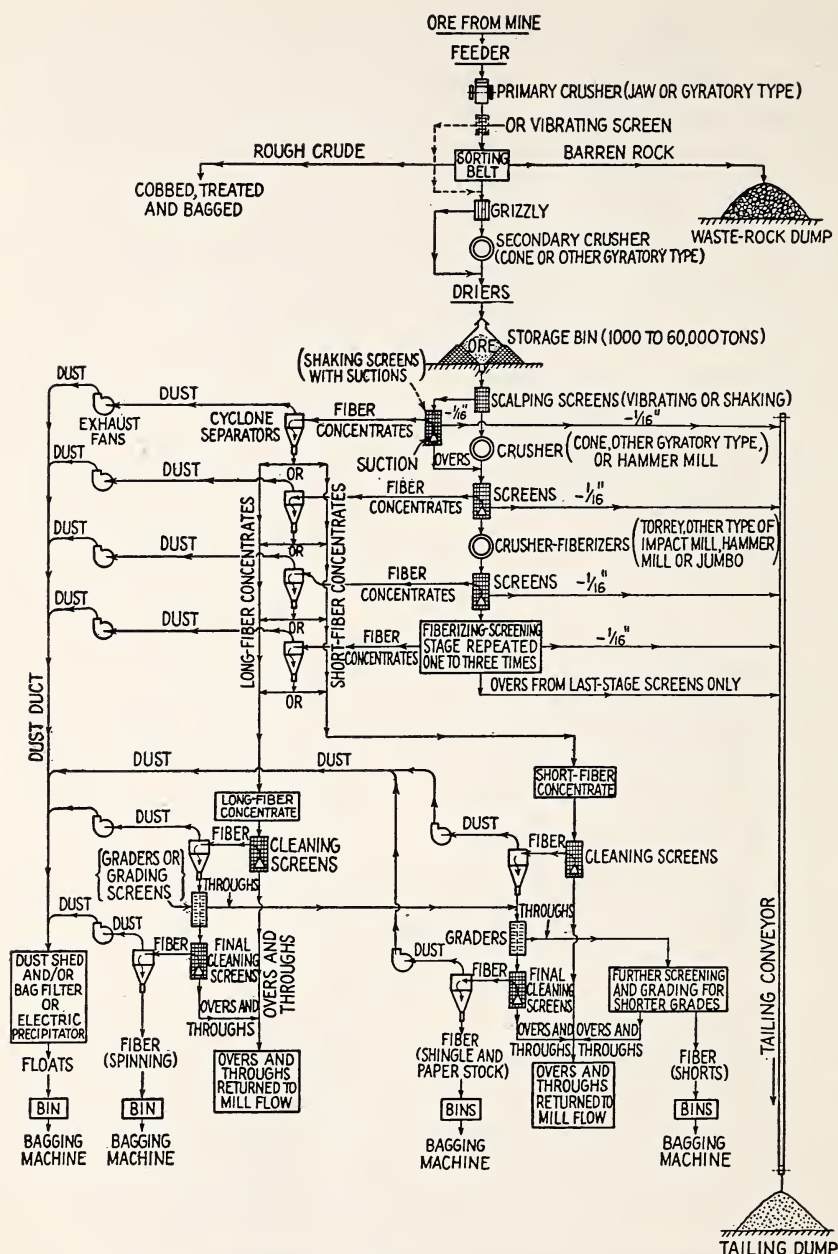


FIG 5—GENERALIZED FLOWSHEET OF CANADIAN ASBESTOS MILL.

of serpentine ore to slip as the crusher jaws apply pressure, resulting in a jumping action by the rock and therefore decreased efficiency.

Driers may be either the conventional rotary kiln type or the vertical stack. The former is of standard design, consisting of a rotating cylinder 40 to 60 ft long by 4 to 6 ft in diameter. The drier may be installed so that the hot furnace gases pass out along the outer shell before returning through the cylinder itself where they are in contact with the ore. For increased efficiency and to lessen the tube-mill action of the larger pieces of ore on the fiber-bearing fines, the drier cylinders sometimes are divided into segments, or smaller cylinders or tubes are built within the main shell, so that the ore and gases are confined to spaces of smaller cross-sectional area, in which there is a better mingling of the two as well as less grinding action on the fiber.

The vertical drier consists of a square stack, generally 7 by 7 ft in cross section by 50 ft high. Ore is introduced at the top and falls through a rising current of heated air together with the gases of combustion from a coal-fired furnace. It is retarded and dispersed in its fall by a gridwork of cast-iron bars throughout most of the height of the stack, requiring about 20 sec to reach the discharge chute at the bottom. Forced draft is introduced under the furnace grates and the gases are drawn from the top of the drier by an induced-draft fan through a cyclone collector, where a small amount of dried fiber and dust is caught, before exhausting into a smokestack.

Storage bins to which the dried ore is conveyed, in addition to serving the normal purpose of a uniform supply of mill feed, allow time for the ore to cool and to lose up to one per cent of the remaining moisture. The bins often are made by depositing two high parallel ridges of mill tailings and constructing a reinforced-concrete tunnel with draw points in the valley between the ridges. The angle of repose of the tailings forms the bin bottom; a steel-frame structure covered with corrugated asbestos provides cover.

Screens, so widely used in an asbestos mill, serve a dual purpose—the normal one of sizing and secondly as planes from which the fiber can be lifted away from the rock by aspiration. For the latter reason a shaking action is preferable to a vibrating action, as it permits the fiber to bed above the rock and to be more effectively separated. Screens usually are constructed in the mine shops. They are made with wooden frames, reinforced where necessary with steel, and actuated by roller-bearing eccentric, although where a long stroke at slow speed is desired ordinary bearings and even a crank-type eccentric may be used. In size they are generally either 4 or 5 ft in width by 11 ft or more in length. The support usually is by pieces of hardwood shaped to allow the necessary degree of flexibility. Screens often are arranged in pairs, back to back, with one eccentric shaft serving both.

Suction hoods are made with an opening of from 2 to 5 in. and are sufficiently long to extend across the full width of the screen. They are suspended above the lower end of the latter and are adjustable as to height. The tapered upper section of the hood converges into an air duct, commonly 15 in. in diameter, which conveys the air to a cyclone collector where the fiber is dropped, and thus through the exhaustor fan. One fan may serve a number of suctions, approximately 15 hp being required for each 15-in. pipe and suction.

DUST COLLECTION

As a considerable amount of dust escapes collection, the air discharged from the fans is conducted usually to a settling chamber, often constructed in the form of a large shed in which there are burlap baffles to assist in the removal of the dust, before the air is exhausted to the atmosphere. These so-called dust sheds, however, are insufficiently effective and in the more populated areas are being supplemented by more positive means of filtration or precipitation. A system of electrical precipitation has proved quite efficient at one large plant but others have favored the use of bag filters. The latter are built in units in which there are commonly 144 to 224 fabric tubes 8 to 10 in. in diameter by 18 ft or more in length per unit. Air is introduced into the tubes from below and filters through the fabric, depositing the dust on the inside surface. Multiple units are built, so that the air supply can be diverted periodically by a timed mechanism and, at the same time, the bags or tubes are shaken mechanically to dislodge the layer of accumulated dust. Accepted practice is to have sufficient fabric area so that not more than 4 to 5 cfm of free air is being filtered per square foot of fabric. For this reason a mill treating 3000 to 4000 tons per day and exhausting some 500,000 cfm of free air requires an extensive filter installation.

CRUSHING AND GRADING

Several other machines are named in the flowsheet (Fig 5), which are little used except in asbestos milling and therefore should have some further mention.

The Torrey cyclone is a machine in which ore previously crushed to 2 in. or less is further reduced by impact. The machine consists of a vertical cylindrical shell 54 in. in diameter by 5 ft high, enclosing a central upright shaft. Ore, fed on the top, falls onto a circular table or "spider" bolted around the shaft and in turn supporting four radiating vanes of manganese steel. Since the whole assembly is revolving at high speed, the material is thrown outward by centrifugal force and is caused to impinge against heavy grooved castings. As the ore falls, it is caught in a conical hopper, which, in turn, guides it to a lower spider

and vane assembly on the same shaft, for a second stage of crushing by impact in the same way.

The Jumbo has a horizontal cylindrical body 3 ft in diameter by 6 ft long. The inside periphery is lined throughout with serrated chilled iron castings. A central horizontal shaft supports a number of arms with heavy detachable wearing tips cast with a beveled face on one side. The feed entering the upper part at one end is subjected to a rubbing and grinding action, as it is moved the length of the machine by the propeller-like action of the beveled tips, and it is discharged through an opening in the bottom at the opposite end.

Graders may be either conventional trommels, or, as the name is generally applied, a modification of this machine in which the cylinder of perforated plate remains stationary and the material (fiber in this case) is moved from one end to the other by arms, clamped to a revolving central shaft and twisted to give the necessary forward pitch. In size these generally are about 7 ft long by 26 in. inside diameter.

TESTS AND SPECIFICATIONS

Canadian asbestos fibers are graded within definite limits and production is controlled by means of the Quebec Standard Testing Machine, which has become the accepted measure of fiber length by which milled asbestos is sold. All grades except crudes, sand and gravels, are controlled by this standard. The machine consists of a nest of four rectangular cast-aluminum boxes clamped onto a table that is shaken by an eccentric. The bottom box serves as a pan and the three superimposed sieves have screens of successively larger meshes. From the top, down, the mesh sizes are: $\frac{1}{2}$ -in. opening, 4-mesh and 10-mesh. All screens and dimensions are to exacting specifications.

To make a test, 16 oz of asbestos is placed on the uppermost tray, which is then covered and tightly clamped. The machine is started and allowed to run at 328 rpm for exactly 600 revolutions, when it is stopped by an automatic device. At the end of this time, the asbestos remaining on each sieve is weighed and the test is recorded to the nearest tenth of an ounce.

The Canadian classification of chrysotile asbestos specifies the minimum shipping test for each grade; i.e., the minimum number of ounces of fiber there shall be on each of the upper screens and the maximum there shall be in the pan. For conveniences of designation, fibers have been divided into numbered groups and each group has been subdivided into grades, identified by letters of the alphabet. Space does not permit an itemization of all the recognized grades but, by way of explanation, in the following list of groups there are a number of grades, each with its minimum guaranteed test, under each group heading. In group No. 3, for example, there are five grades, the longest of which

is 3F with a guaranteed test of 7-7-1 $\frac{1}{2}$ - $\frac{1}{2}$ (i.e., ounces on screens of $\frac{1}{2}$ -in., 4-mesh, 10-mesh, and pan, respectively, the whole adding up to 16.oz). The shortest grade in this group is 3Z with a test of 0-8-6-2.

- Group No. 1. Crude No. 1 ($\frac{3}{4}$ -in. staple and longer).
- Group No. 2. Crude No. 2 ($\frac{3}{8}$ -in. staple up to $\frac{3}{4}$ -in.).
- Group No. 3. Textile and spinning fibers (testing 0-8-6-2 and over).
- Group No. 4. Shingle fibers (testing below 0-8-6-2 and including 0-1 $\frac{1}{2}$ -9 $\frac{1}{2}$ -5).
- Group No. 5. Paper fibers (testing below 0-1 $\frac{1}{2}$ -9 $\frac{1}{2}$ -5 and including 0-0-10-6).
- Group No. 6. Waste, stucco, or plaster fiber (testing 0-0-7-9).
- Group No. 7. Refuse or shorts (testing 0-0-5-11).
- Group No. 8. Sand—a mill product weighing less than 75 lb and more than 35 lb per cu ft.
- Group No. 9. Gravel and stone—a mill product weighing more than 75 lb per cu ft.

MARKETING

A great part of all raw asbestos produced is from the mines and mills of companies that also manufacture asbestos products. Independent producers, meaning those that deal in the raw products only, are in the minority. For much of the output, therefore, the producer is likewise the chief consumer, and marketing is less of a problem than for many commodities. It would be misleading, however, to confine ourselves to this generalization, since, in fact, there are still substantial tonnages sold to other manufacturers by the mine-to-finished-product companies, as well as by the independent companies that produce the raw fiber only.

Agencies and representative firms handle part of the business of marketing and often act as jobbers for the distribution of small lots. With this exception, nearly all fiber is shipped direct from mine to consumer.

The asbestos as it is produced is packaged in jute or heavy paper bags containing 100 or (occasionally) 125 lb, and generally is shipped in boxcars of 30 to 50 tons.

Sales are made on the guaranteed test as previously described, which is the accepted, although empirical, method used as a measure of fiber length, prices being based largely on length. In this connection there is also to be considered, however, what may be called the potential test as well as the actual test of the fiber at time of shipment. To illustrate, we might compare crude with a milled fiber, as an example. Crudes are not sold on test and if we were to determine the value of, say, a No. 2 crude by the relative amount retained on the upper sieve of a testing machine, it would fall much lower in the price scale than its actual value. The difference is that the crude is still in lumps, many of which can pass through the $\frac{1}{2}$ -in. screen opening. On the other hand, when this crude is received at the consumer's plant, it is further processed so that the individual fibers are pulled apart, converting the product from a collection of lumps to a fluffy fibrous mass, which would then virtually

all remain on the top box of the testing machine. Now this same principle may be applied to a lesser degree in comparing mill fibers, since these may be in some cases recovered under conditions that will leave the fibers in a relatively less "opened" or "harsher" state. The classification and test under which two grades of asbestos are sold may therefore be identical but one may contain more pieces of "crudy" fiber. The result is that when the fiber in the less opened state is received at a consumer's plant, it can be further processed and, in the final state of preparation, it will be equal in test to that of a higher grade. Because of this "potential," the more "crudy" fiber may therefore command a price premium above the average mill fiber of that grade. At some mines it is practical to produce fibers in this way, particularly the shingle grades. European users generally prefer these more "crudy" fibers, partly because of the lesser bulk and consequent saving in ocean freight. Consumers in the United States, on the other hand, generally prefer grades that are ready to use with a minimum of handling and preparation at their plants.

USES OF ASBESTOS

There are many characteristics, of course, which affect the usefulness and value of asbestos. In the longer grades for spinning purposes, the fine, silky chrysotile fibers of high tensile strength are most in demand, while coarser, more brittle fibers may have but a limited use. Even what is generally considered high-quality chrysotile from serpentine deposits is not entirely suitable for insulation of electric equipment because of a small percentage of adhering magnetic iron oxide, and, for this reason, chrysotile occurring in dolomite, such as the Arizona fibers, is more suitable for this purpose. Some grades of tremolite and other amphibole fibers are particularly suited for filters and similar applications where a high degree of resistance to acid is required. In the short grades of chrysotile, when these are for compounding with oils or resins, the relative ability to absorb oils, and the wet bulk, are often characteristics examined by the plant chemist.

The uses for asbestos are many and diverse and space will not permit enumeration except of a summary nature. Much of the longer fiber is spun into yarn for the weaving of cloth, brake lining and other articles. Some is also used for special packings, gaskets, and insulating materials. The building trades, led by asbestos cement products, consume by far the greatest tonnages. Fibers of medium length, to the extent of 15 pct or more by weight, are mixed with portland cement to manufacture shingles, corrugated and flat sheets, and pipe. To this may be added asphalt asbestos shingles and siding, which generally are made with a somewhat shorter fiber than the cement products. Further,

asphalt asbestos floor tiles, in which large quantities of short fibers are now being absorbed, may be included.

In the automobile industry, clutch facings and brake linings account for large quantities of the medium length and shorter fibers as well as the smaller percentage used for the woven linings. Other important uses are for gaskets, packings and asbestos paper.

In the insulating field, much paper-stock asbestos goes into air-cell steam-line insulation, while in 85 pct magnesia block insulation approximately 15 pct of a longer grade of fiber is mixed with magnesia and molded and cut to required shapes. A type of sprayed insulation, which was used in ships during the second World War, is finding new application for acoustic insulation.

The war developed a tremendous demand for high-grade spinning fibers for use in ship, tank, and aircraft construction, and markets for these were under close government control. Special compounds in which asbestos was incorporated were developed for waterproofing vehicles taking part in beach landings and crocidolite fiber was required for gas-mask filters.

With the progress of industry, more short-fiber asbestos is being used than ever before. Much is compounded with various synthetic resins in the manufacture of molded articles, also with asphalts and oils for cements, tiles, and linoleum; with plastics, paints, and greases.

In recent years, the glass industry has made progress in the production of fiber-glass and the manufacture of attractive fabrics from this synthetic fiber. Blended with asbestos, fiber-glass is finding application for insulation of electrical equipment. Mineral and slag wool has become a useful commodity, which is widely used as space insulation in the building trades and in other industries, where it is particularly suited because of its nonhygroscopic nature. These products, and some of the vegetable fibers and wood flour, may be thought of as asbestos substitutes, but, in fact, they are for the most part simply substances for which somewhat similar uses are found, and each has its place and usefulness.

PRICES

Prices of the numerous grades of fiber cover a very wide range. At the first of this year (1948) floats and other very short grades were selling at \$27 or less per ton; cement stocks from \$31 to \$46; paper stock at \$70 to \$80. Shingle fibers range between \$100 and \$130 and spinning grades are generally between \$200 and \$300 a ton.

Canadian crude prices for the past 10 years have remained relatively stable; No. 1 crude, for example, from 1938 through 1945 was \$700 per ton in Canadian dollars, although having risen to \$800 in 1946.

On the whole, prices for asbestos fiber maintained a gradual in-

crease throughout the period 1936–1946. During the war years, Canadian asbestos was placed under federal price control and from 1942 through 1945 prices were frozen. It was inevitable that, in the face of greatly increased costs, the Canadian producers were forced to raise prices in 1946 and again in 1947. Meanwhile prices for African asbestos have also risen.

The graph of Fig 6 shows average values based on annual sales for Canadian No. 1 crude, spinning and shingle fibers according to statistics published by the Quebec Bureau of Mines. The price range of Rhodesian No. 1 is estimated from available data.

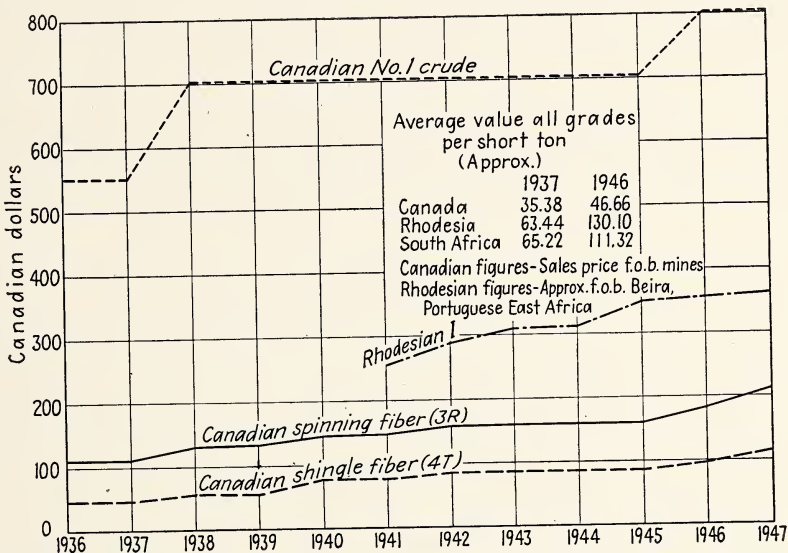


FIG 6—YEARLY AVERAGE VALUE PER TON OF VARIOUS GRADES OF ASBESTOS FIBER, IN CANADIAN DOLLARS.

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CHAPTER 3

BARIUM MINERALS*

BY F. J. WILLIAMS†

BARITE, naturally occurring barium sulphate, is the chief barium mineral that is produced commercially. Barite is also called "barytes," "heavy spar," sometimes "baryta" and, locally in Missouri, "tiff."

Pure barite is white, opaque to transparent. It crystallizes in the orthorhombic system, frequently with twinning. Impurities cause a wide variation in color, commonly buff, gray and white with irregular reddish iron stains. Less frequently found are shades of yellow, green, blue, brown, and black. The rock is brittle and breaks with an uneven fracture, although specimens from some of the residual deposits, particularly in Missouri, appear to have a cleavage due to the separation of the different layers of deposition. The hardness varies from 2.5 to 3.5 on Mohs' scale and different localities are said to produce either "hard" or "soft" barite. This generally refers to the ease of grinding of the product. The specific gravity of pure barite is 4.5 and this will vary downward, depending on the impurities present. The mineral has a white streak and a pearly to vitreous or sometimes stony luster. Pure barite contains 65.7 pct BaO and 34.3 pct SO₃.

Witherite, native barium carbonate, is not mined in the United States at the present time although a number of occurrences have been reported. A small quantity of witherite has been removed from a mine at El Portal, California, but the area high in witherite was small and soon depleted. The bulk of the deposit is predominantly barite. Great Britain is the world source of witherite and small quantities are imported into the United States.

DISTRIBUTION OF DEPOSITS

Occurrence of barite is widespread; it has been reported on all the continents and in all the major countries of the world. Deposits vary from those containing millions of tons down to scattered rock fragments

* Adapted in part from the chapter on Barium Minerals by W. M. Weigel in the first edition of this book (1937).

† Technical Director, National Lead Company Research Laboratories, Brooklyn, N. Y.

and vary in purity from almost pure barite to very low-grade impure material. Workable deposits are chiefly of two types:

1. Veins of total or partial replacements of dolomite and limestone. In some localities replacements occur as bedded deposits due to the complete replacement of sedimentary beds. Where the original carbonate rock was a seam or vein in a shale or sandstone, the barite replacing it may appear to have replaced the shale or sandstone, but such replacement is not believed to take place.

2. Residual deposits in clays derived from the weathering of barium-bearing rock such as dolomites, usually derived from type 1. In addition, barite occurs as a gangue mineral in metalliferous ore bodies. Such deposits are reported to have been worked actively in the 1930s in southern Spain. However, such procedure is not general at this time. It may be possible that with the developments in barite recovery by flotation, a barite fraction can be removed if flotation is employed for the beneficiation of metalliferous ore.

Both types of deposit are important from an economic standpoint and are sources of production throughout the country. The choice of deposit to be mined is not a question of its geology but rather of its geography. Nearness to the consuming area is the most important factor, followed by nearness to rail transportation and then by the adaptability of the deposit to mining by conventional methods without excessive mining costs. This is particularly well illustrated by the deposit in Arkansas, which is one of the first class. Arkansas grew from a nonproducing state to be the chief producing state in a few years because of the proximity to the large market in the Gulf Coast oil fields. Improved mining and concentrating techniques of course have influenced greatly this type of development and account for the fact that in the early stages of the barite industry in this country a large percentage of the mining was from residual deposits in Missouri, Georgia, and Tennessee.

United States

Arkansas—The principal producing locality of Arkansas is the Magnet Cove area, near Malvern, Hot Spring County. The barite occurs in a plunging synclinal fold of the Stanley shale of Pennsylvanian age, as a replacement for limestone with the less soluble shale, flint, and chert remaining dispersed through and mingled with the barite. Approximately 100 acres is underlain by the main deposit, and the reserves, partially outlined by diamond drilling, are estimated at several million tons. Other occurrences, some of them rather large, are known in the Magnet Cove area but their extent has not been determined and no development has been attempted. Barite has also been proved in the Fancy Hill district of Montgomery County, which constitutes an additional ore reserve, although to date there has been no production in that locality.

At the present time there are two mining operations in the ore on opposite converging wings of the syncline, each consisting of several workings following richer portions of the ore body. The ore varies in color and may be red, yellow, gray or green. The composition is variable across the deposit and may range from 50 to 70 pct barium sulphate, the remainder being chiefly silicates. While this deposit has been known for a considerable time, it had little commercial value until a neighboring large market developed in the Gulf Coast and beneficiation by froth flotation was introduced.

Missouri—The barite occurring in Washington County, Missouri, is probably one of the best known and completely described residual deposits in the United States. The barite occurs in a clay mantle covering the underlying dolomites. These dolomites originally contained the barite in the form of veins and the weathering of the rock left the relatively insoluble barite dispersed in the residual clays. Deposits on the Potosi formation of the Cambrian are the most important but the overlying Eminence formation accounts for some of the ore. The deposit consists of loose fragments of barite with chert, drusy quartz and dolomite boulders embedded in the red clay. In certain formations some of the larger fragments are concentrated near the bottom, or even on bedrock. The clay mantle varies in thickness from 0 to 30 ft. Single areas of 100 acres or more may be entirely ore-bearing but usually there is a concentration of the barite in runs or "leads" 10 to 20 ft wide and several hundred feet long. While the barite often is found at the grass roots and is exposed in plowing, the usual section consists of a foot of surface soil followed by about 2 ft of chert, gravel and clay. Below that a 3 to 4-ft stratum contains barite, chert and quartz in the clay, below which lies another 4 ft of barite-free clay. Below that is the largest concentration of barite, with chert and dolomite, in red clay extending downward for several feet. More red clay separates this stratum from the bedrock.

The barite is pure white on fracture, while the surfaces and cleavage planes usually are coated or stained with limonite. Galena is associated with the barite and well-defined crystals of galena frequently are completely encased by barite.

In the central Missouri district, the residual deposits usually are found in clays at the top of the Gasconade formation, the top member of the Cambrian, and sometimes on the Roubidoux, the bottom of the Ordovician. The occurrence is similar to that in Washington County except that the deposits are deeper and more restricted horizontally. The ore in Washington County is one of the softest in the country; that in central Missouri is a harder variety and is less stained with limonite.

Georgia—Georgia has enjoyed considerable eminence in the past as a barite-producing area but some of the deposits have been depleted and only the Cartersville district, Bartow County, remains active. The

Cartersville deposits occur in clays derived from the weathering of lower Cambrian, particularly the Weisner quartzite and shaly limestone of the Beaver formation. The barite originally was deposited in fractures and cavities in the rocks. Some of it was possibly a replacement of part of the limestone. On weathered portions of the limestone, containing veins and replacement bodies of barite, it is indicated that the barite in the clay has been freed from limestone during the process of weathering. The deposition of the barite in limestone occurred in and adjacent to fault zones.

There are also deposits in Polk, Floyd, Cherokee, Gordon, Murray and Whitfield Counties, some of which have been mined in the past.

Because of the increased thickness of overburden, up to 50 ft, found over some of the Georgia deposits, some of the mining operations were moved to Missouri in 1945.

Tennessee—Barite is mined in Tennessee near Sweetwater, Monroe County, and in Cocke County. The Sweetwater district is the more important and has been mined for a considerable time. The barite occurs there as a residual deposit in clay formed from the weathering of the Knox dolomite of Cambro-Ordovician age. Barite also occurs in the unweathered Knox underlying the residual clay. Workable deposits in this area are scattered and there appear to be three major "veins" from 100 to 300 ft wide and 60 to 80 ft deep extending 10 to 15 miles. The barite is both hard and soft and frequently is coated with limonite. Chert and fluorite are the chief associated minerals and the presence of the fluorite prevents the production of high-grade barite in portions of the areas, inasmuch as the fluorite is not readily separated from the barite.

The barite in Cocke County occurs in irregular fissures and as replacements of limestone "veins" in the shales and sandstones of the Cambrian age. Although these deposits are being actively worked, the barite is associated with fluorite and chert, which make the ore unsatisfactory for many uses. The absence of iron-bearing minerals, however, leaves a product that is suitable for use in glass, since the fluorite and chert are not harmful for that purpose.

Barite also occurs in Fentress, Davidson, DeKalb, Dickson, Smith, Trousdale and Wilson Counties.

California—The barite in California is generally in the form of lenticular deposits formed by the replacement of limestone. It is being mined at El Portal, Mariposa County; Washington, Nevada County; Auburn, Placer County, and Greenville, Plumas County. The deposit at El Portal is of chief interest in that it has been mined since 1910. For many years it was the only producer of barite on the west coast. Further, the deposit is a mixed barite-witherite ore. A series of lenses occurs on both sides of the Merced River. The material on the north

side of the river is generally richer in witherite and at one time a small quantity of high-grade witherite was hand-picked from the ore mined in this area. The rest of the ore on the north side of the river is mixed barite and witherite with the sulphate content increasing proportionately to the distance down from the apex of the ridge. This is understandable in light of the mode of deposition of the deposit. It is believed that calcite was replaced by witherite and that subsequently the witherite was replaced by barite by percolating sulphate waters. The lenses on the south side of the river are chiefly barite containing a negligible amount of witherite.

Barite also occurs in Inyo, Los Angeles, Orange, San Bernardino and Santa Barbara Counties.

Nevada—There has been a small production of barite in Nevada for 10 years or more. There are some very large deposits of high-grade ore, mostly bedded deposits replacing limestone, but production has been small because of the distance from rail shipping points and also because the limited demand on the west coast was satisfied by the production in California. Now production in California appears to be decreasing and that in Nevada to be increasing.

Four mines in Nevada are producing barite: (1) at or near Argenta and (2) Battle Mountain, Lander County, (3) Carlin, Elko County, and (4) Tonopah, Nye County. All are generally vein deposits in limestone or shale. The output of these mines is used to augment that from California for the Pacific Coast area.

Other States—Barite was first mined in Virginia in 1845 and until about 1890 Virginia was the chief producing state. Barite occurs as both residual and unground deposits in country rock, in Campbell, Pittsylvania, Roanoke, Fauquier, Botetourt, Russell, Tazewell, Smyth, Bedford and Grayson Counties.

The North Carolina barite has been mined in the Hot Springs area, Madison County, and in the Kings Mountain area, Gaston County. It occurs as veins in fractured granites in the former locality and in siliceous sericite schist in the latter.

In the early 1900s barite was mined in Kentucky, where considerable ore occurs in the central part of the state. Most of the barite is associated with fluorite, from which it is impossible to separate it, and which makes the deposits less valuable for most uses. A mixed barite-fluorite ore is being mined for use in glass.

Barite was mined in Alabama in the early 1900s from residual deposits. The deposits are reasonably extensive and represent a possible future reserve.

There has been intermittent production of barite from vein deposits near Kings Creek, Cherokee County, South Carolina, for 50 years.

Barite has been mined spasmodically in Alaska and Connecticut

and it has been reported in many other states. Large lenticular deposits have been reported in northeastern Washington but as yet they are undeveloped because of remoteness from markets.

Foreign Deposits

Most foreign countries have deposits of barite but only Canada, Cuba, Germany, Italy, Great Britain, and the USSR have important production from the standpoint of world trade.

Since 1942, Canada has been one of the chief producers of barite, when a large body of high-grade, light-colored barite ore was opened up at Pembroke, near Walton, Hants County, Nova Scotia. The ore is very close to tidewater, which facilitates the exporting of both crude and ground barite. A large tonnage of ground barite has been shipped to Trinidad and Venezuela for oil-well drilling. Barite has also been exported from Canada into the United States to make good the deficiency caused by the loss of imports from Germany. Some barite is produced at Golden, British Columbia.

Cuba produces barite in the provinces of Oriente and Pinar del Rio. The output formerly was ground at Regla, near Habana, for export to Trinidad and the United States, but there has been little or no export trade during the past five years.

Before 1939 Germany was the chief producer of barite, supplying nearly half the world output. The principal deposits were the Meggen, in Westphalia. Other barite occurred in Hessen, Thuringia, Bavaria, Baden and Silesia. The ore occurs chiefly in veins and is recovered by underground mining. Between the two late wars, most of the United States imports came from Germany, chiefly from Meggen. Imports probably will be resumed when trade is stabilized unless the ore from Nova Scotia is able to completely supplant the German barite.

Italy produces barite from a number of small deposits and from time to time has exported barite to the United States.

Barite is mined in western Ireland and exported to Great Britain.

Production of barite in the United Kingdom has increased since 1939 because of the unavailability of barite from Germany. Large deposits occur in Ayr, Devon, Shropshire and Derby Counties. The world supply of witherite comes from the deposits in Northumberland County, in the north of England.

Little is known about barite production in Russia, although a number of deposits have been reported.

Greece, France and Spain produce barite in some quantity and have exported to the United States. Australia and Korea produce barite.

A source of barite has been worked recently near La Rosita, Coahuila, Mexico, and a small quantity has been exported to the United

States. Other occurrences have been reported in the states of Sonora, Chihuahua and Nuevo Leon.

Brazil has one mine operating on Camamu Island, off the coast of Bahia, producing for oil-well drilling in Brazil and Venezuela.

POLITICAL AND COMMERCIAL CONTROL

Most of the principal consuming countries of the world have sufficient supplies of barite for their own use but there is some international flow of crude and ground barite. This flow is based chiefly on cost at the point of consumption rather than on any other factor. While the United States has ample reserves to take care of its needs, in recent years production facilities sometimes have been strained to meet this need. This factor has added to the economic factor in determining imports along the Atlantic seaboard, where normally the delivered price for the imported barite is lower than that of the domestic barite from Missouri or Georgia. During the war years, when production facilities in the United States were strained, importation of barite was difficult because of shipping conditions.

The United States and Germany were the two largest producers. In the early 1930s the production in the two countries was approximately the same but in the middle and late 1930s German production exceeded that of the United States. Statistics on German production during the war years were not completely available but it is evident that production in the United States from 1940 on has exceeded that of Germany.

Canada, United Kingdom, Italy, USSR, and Greece are worthy of mention as having nominal production of barite. The production in Canada, chiefly from Nova Scotia, increased very rapidly in 1944 and 1945 and has become a factor in world trade, particularly in the western hemisphere. At present, the entire political situation is still in a state of flux as an aftermath of the war and it will be some time before the normal trade in barite is readjusted. United States imports in 1946 were chiefly from Canada although a small tonnage was obtained from Mexico.

The United States Tariff Act of 1930 provides a duty of \$7.50 per long ton on ground or manufactured barite and \$4.00 per long ton on crude barite, equivalent to \$3.57 per short ton.

PRODUCTION AND CONSUMPTION

Barite production in the United States started in Fauquier County, Virginia, about 1845. Production in Washington County, Missouri, began between 1850 and 1860. European production probably predates that of the United States by many years. The last 25-year period has seen a marked increase in the demand for barite, which has, of course, been reflected in the production. Fig 1 shows graphically the gradual

upward trend of production and production plus imports, corresponding to consumption, over the last 16 years. World production has of necessity been omitted because of the paucity of data during recent years. It is estimated, however, that the United States production since 1944 has exceeded that of the rest of the world combined.

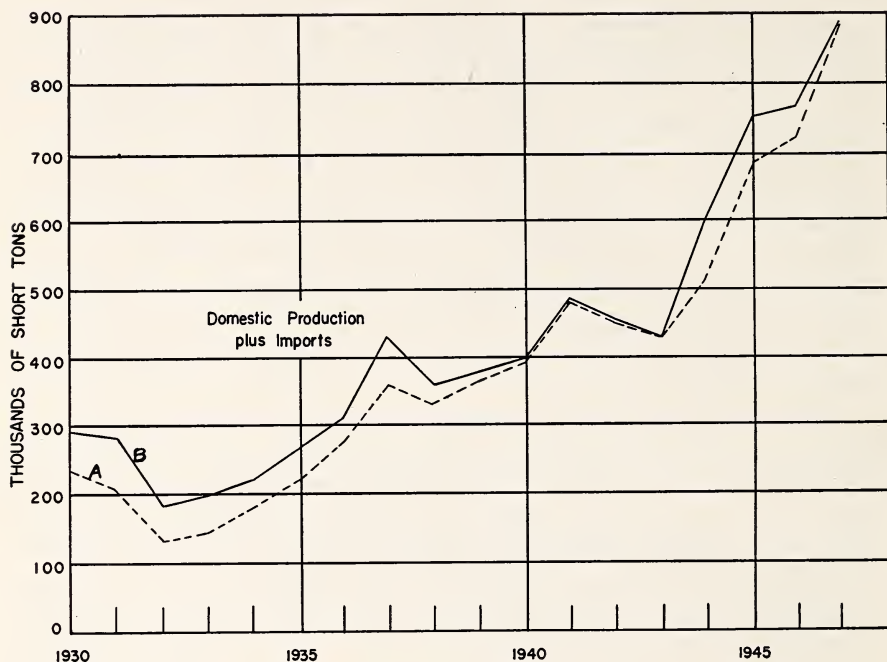


FIG 1—PRODUCTION OF CRUDE BARITE.

A, production; B, production plus imports. All statistics from Minerals Yearbook, U. S. Bureau of Mines, 1932–1933 to date.

Of considerable interest in the production from the United States is the recent large tonnage developed in Arkansas. Prior to 1941, little or no barite was mined in Arkansas and no statistical data were kept with reference to the output. Table 1 shows the tonnage produced in Missouri, Georgia, and Tennessee since 1938 and in Arkansas since 1944, the first year in which detailed statistics were kept. It is of interest to note that since 1944 Arkansas has been the chief producing state, exceeding Missouri, which had been the chief producing state since about 1890. As mentioned before, the factors influencing this have been the concentration of the Arkansas barite by froth flotation and the proximity of this deposit to the consuming areas in the oil fields of the Gulf Coast.

PROSPECTING AND EXPLORATION

Prospecting for barite is both simple and inexpensive in most localities. After the district where the ore is known to occur has been ex-

plored in a general way, the most favorable areas are selected for prospecting. Residual deposits in clay are prospected by driving a pointed steel rod into the clay, to bedrock if possible. If the rod penetrates barite, the ore adheres to the rod and shows white streaks when the rod is withdrawn. Chert and rock only scratch the rod. Test pits or drill holes are sometimes sunk following the rodding. Drilling has replaced test pits to a large degree in recent years.

TABLE 1—*Domestic Crude Barite Sold or Used by Producers in the United States*
SHORT TONS

State	1938	1939	1940	1941	1942	1943	1944	1945	1946	1947
Arkansas.....	^a	^a	^a	^a	^a	^a	159,686	260,660	288,286	376,017
Georgia.....	64,304	86,589	92,302	104,446	86,636	98,680	108,851	110,393	69,274	61,202
Missouri.....	156,539	171,642	179,455	212,718	146,270	124,147	150,748	225,467	270,850	291,619
Nevada.....	^a	^a	^a	^a	^a	12,157	22,390	28,919	^a	37,388
Tennessee.....	29,898	57,140	70,767	104,511	83,291	52,593	43,033	32,812	33,595	31,476
Other states.....	58,922	68,238	66,829	81,481	113,287	132,766	33,909	37,811	62,357	36,380
Total.....	309,663	383,609	409,353	503,156	429,484	420,343	518,617	696,062	724,362	834,082

^a Included in other states.

Prospecting of vein deposits often is done in the usual manner by trenching across the vein outcrop, sinking prospect shafts, and tunneling when the topography permits; more recently, diamond drilling has been used, and constitutes the most satisfactory method of properly outlining the ore bed both as to extent and composition.

MINING METHODS

Until 1941, the bulk of the production in the United States was from residual deposits and the methods employed were similar at all locations. Initially, the residual deposits were worked by hand mining, particularly in Georgia and Missouri. Mechanical methods started to replace the hand mining about 1920 but the latter continued in Missouri until about 1940.

A large amount of ore was removed from the Missouri area by hand mining, which was interesting in its methods and picturesque in its practice. The hand miner sank a vertical shaft in the clay, 4 to 5 ft in diameter, throwing out dirt until the shaft became too deep. At greater depths, the dirt was removed by a hand windlass and bucket and at the ore level an excavation was made in the form of an inverted mushroom. Generally no piling or cribbing was used. The shafts usually were 10 to 15 ft deep, although some were sunk to 30 to 40 ft. The barite was separated from the clay at the surface and cleaned by hand, dried over open fires where necessary, and the residual dry clay was shaken off in a "rocker" or "rattle box."

Four general methods of mining and recovering barite are followed. Listed in the order of importance, they are:

1. Barite-bearing clay is dug with power shovels in opencuts after the overburden has been removed. The clay is separated in log washers and the nonclay fraction is further concentrated by jigging and other processes. This method is practiced in Missouri and Georgia and to some extent in Tennessee.

2. Barite-bearing shale is quarried in open pits by blasting and the barite is recovered by flotation. This method is used in only one deposit, in Arkansas.

3. Underground barite veins are mined by standard methods and the ore is beneficiated where necessary. This is used in California and Nevada and to some extent in Tennessee. One producer in Arkansas is preparing for underground mining.

4. Massive barite is quarried in open pits by blasting, with little or no subsequent sorting, in Nevada.

Mechanical Mining

Power shovels and log washers have replaced the hand miners in areas where the barite is a residual deposit in clay. In Georgia and Tennessee, this started during World War I because of high labor costs, and in Missouri during the late 1920s. Since 1939, there has been very little hand mining, most of the operations having been mechanized.

In Georgia and Tennessee, the overburden is stripped by means of power shovels or scrapers. In some places in Georgia the overburden is as much as 50 or 60 ft deep. Once the overburden is removed, power shovels mine the barite-bearing clay and load it into trucks, which carry it to the washer. The washer is not a permanent installation and is moved periodically to follow the working shovels, so that the truck haul is not allowed to exceed approximately one mile.

The trucks dump the clay into a receiving bin, the bottom of which is a grizzly, and the clay, rock and barite are washed through the grizzly with a stream of water. Lumps that are too large to pass the grizzly are rejected unless they are barite; barite-bearing lumps are broken and allowed to fall through the grizzly. The slurry from the grizzly falls into the log washer, usually a 27 to 30-ft unit with double logs rotating in opposite directions. The clay mud overflows the log washer and is allowed to run or is pumped to the mud pond. The discharge passes through a trommel and the oversize is crushed or hand-picked. The barite is separated from the rock on jigs. Iron is sometimes removed magnetically. Somewhere between 5 and 15 pct of the total barite in the clay is lost as fines in the overflow. Some attempts have been made to decrease this loss of fine material.

Mining in southeast Missouri is similar but less difficult. There is

little if any overburden in the Missouri area and it is generally neglected. Where it is stripped off, the work is done with a dragline or a tractor-carryall unit. The concentration of barite in the clay is somewhat higher than in Georgia or Tennessee and follows definite runs, which the shovel operator can follow with comparative ease. The Missouri barite is softer than the Georgia barite and is completely disintegrated in the trommel. The trommel itself is simply a rotating iron cylinder about 6 ft long and 4 ft in diameter with many holes approximating $\frac{1}{2}$ in. in diameter. The barite is shattered and passes through the trommel screen, while the quartz, dolomite and hematite continue through to the discharge end, except for the finer fraction. The fine quartz and dolomite are separated by jiggling. Frequently galena is present, which separates out in the first jig cell and may be further concentrated. Hematite does not separate from the barite in the jigs because of the similarity in specific gravity. If a low-iron product is desired, an area where the quantity of iron present is low is selected for shovel operation. Areas that have been completely worked over by hand miners and abandoned have subsequently been mined mechanically, since the hand miners remove less than 10 pct of the available ore and their continued working in that area showed it to be a rich deposit. This fact has minimized prospecting to a considerable degree.

Mining for Flotation

The recovery of barite by flotation started commercially in 1941 and is now second only to the use of log washers as a means of producing barite. It is practiced in two plants at Malvern, Arkansas, where the ore is intimately mixed with quartz, some iron oxide and residual shale. The ore averages 50 to 70 pct barium sulphate, the remainder being chiefly silica. The ore is mined in open pits by blasting. The broken ore is loaded on trucks with power shovels and carried to the plant, where it is crushed. At one plant, the crushed ore is jigged before subsequent grinding. The crushed ore is wet-ground in ball mills to pass 325-mesh. This slurry goes to the flotation cells.

Underground and Open-pit Methods

Three mines employ underground vein operations in the production of barite: (1) at El Portal, California, (2) near Carlin, Nevada, and (3) near Burnett, Tennessee. Generally, the ore is obtained by conventional underground mining operations such as drifting and stoping. The ore is blasted, crushed in two steps, jigged to separate the gangue and ground in a ball mill.

At two deposits in Nevada and one in California barite is mined from open pits. The method is readily applicable to lenticular deposits.

The overburden is removed by stripping, the barite is blasted down and loaded into trucks. The ore is hand-sorted and at one deposit where impurities are abundant further beneficiation is employed. This consists of crushing the material through a jaw crusher and discarding the fines passing a 1-in. screen.

PREPARATION FOR MARKET

Barite is sold in the form of crude lumps, jig concentrates, flotation concentrates, and ground barite. Lump ore generally is prepared from vein or lenticular deposits and is essentially a product of hand sorting. The bulk of the barite produced, however, is in the form of jig concentrate or flotation concentrate. Jig concentrate is produced extensively in Missouri, Georgia, and Tennessee from residual deposits.

In most instances the preparation depends on the end use for which the barite is intended. Barite for oil-well drilling is ground to pass 325-mesh; that to be used for the production of lithopone and barium chemicals is usually sold as jig concentrate, since the minus $\frac{1}{2}$ -in. material is the proper size for subsequent reduction to black ash. Crude lump is acceptable, of course, but the consumer must then crush the lump. The barite for use in glass is crushed to pass 10 or 20-mesh and if the quantity of iron present is high it is removed by magnetic separation. Acid bleaching was formerly employed for the production of barite to be used in glass but this practice has been discontinued. Barite for use as a filler is crushed to pass 325-mesh. If color is important, as in paint, the barite is bleached with an acid treatment to remove the objectionable iron stain. Other treatments are used to remove other objectionable coloring materials, such as pyrite and galena.

Minus 325-mesh barite may be produced by either wet grinding or dry grinding. Where iron is not a factor, the barite is ground in ball mills and the choice between wet and dry grinding depends upon the other operations involved. If the ground material is to be concentrated by flotation, wet grinding is the obvious choice. If the mill feed has been concentrated by jigging, it is simpler to continue with the material wet. Also, if the barite is to be subsequently bleached, it is wet-ground. In Georgia and Missouri, some barite is ground dry. All of the ground barite is bagged automatically in standard paper bags holding 100 lb except bleached barite, for which a 50-lb unit is used. Almost all the bleached barite is made from Missouri ore because of the ease of grinding coupled with the fact that it is readily bleached.

Two flotation processes are employed. One process floats barite from the gangue while the other depresses the barite and floats the gangue. The concentrate is filtered, dried and calcined to remove the flotation agents. The concentrate is high in barium sulphate and is used exclusively for oil-well drilling. The efficiency of the method is attested by

the fact that the output of these two plants makes Arkansas the largest producing state in the United States.

Tests and Specifications

There are no standard tests or specifications for barite. The specifications vary with the end use and the wishes of the consumer. For the production of lithopone and barium chemicals, the most common specification is that the product shall contain 95 pct BaSO_4 and not over 1 pct Fe_2O_3 . The size of product is usually specified by the consumer.

Barite for use in the preparation of drilling muds in the drilling of oil wells is specified generally to have no more than a 5 pct residue on 325-mesh screen. Some consumers specify that the extreme fines shall not be excessive. The only other specification is that of specific gravity, which varies according to the deposit being worked. Generally, a specific gravity exceeding 4.2 is desired, although considerable material has been used with a specific gravity in the neighborhood of 4.0.

Barite for use in glass is specified as having no residue on a 10 or 20-mesh screen and often with no more than 40 pct passing a 100-mesh screen. It should not contain more than 0.2 pct Fe_2O_3 . Some specifications demand an even lower Fe_2O_3 content, although this is not extremely important, because in the ratio in which the barite is used in glass, the amount of iron introduced into the glass by the barite is negligible. Some glass manufacturers prefer extremely fine barite and have used bleached barite as well as that prepared for use in oil-well drilling.

Barite for use as a filler is generally specified to have no more than a 5 pct residue on 325-mesh screen. Specifications as to color usually are relative, it being necessary to meet the color of a standard mutually agreed upon by the producer and the consumer.

MARKETING AND USES

There are two broad markets for barite—ground barite for various uses and crude barite principally for the production of lithopone and barium chemicals. The principal consuming areas are the Gulf Coast, eastern states, central states and California. All these areas consume barite for the two general uses mentioned. The barite produced in Georgia and Tennessee is marketed largely on the Atlantic seaboard and in the eastern states. Imports are largely confined to the eastern states. In the absence of cheap barite imported from Germany, nearly all the barite mined in Georgia and Tennessee is consumed for lithopone and barium chemicals in West Virginia and on the Atlantic seaboard. Recently some barite has been imported from Nova Scotia, which

has helped to offset a corresponding decrease in the production of Tennessee.

Imported barite will thus tend to influence, to some extent, the market conditions in the eastern and central states. Barite produced in California and Nevada is consumed chiefly in California for well drilling and the production of lithopone and barium chemicals. This area is generally self-sustaining with regard to barite. In the central area the producing states are Missouri and Arkansas, the Arkansas barite being sold entirely for well drilling in the Gulf Coast area. Missouri barite is also consumed for well drilling in the Gulf area and for making bleached barite, barium chemicals and lithopone in Missouri, Illinois, and Kansas. Barite for glassmaking in the central states is obtained from Missouri usually and in the eastern states from Tennessee and Georgia.

Table 2 shows the consumption of barite by the major consuming industries. In 1938, for the first time, detailed data were kept on the use of ground barite in the preparation of oil-well drilling muds. Since that time this use has continued to expand so that it is now by far the largest single use of barite. It is interesting to note that the other uses of barite have shown very little, if any, increase since 1941 and that the total increase in consumption of barite is due almost entirely to increased demand for oil-well drilling material.

TABLE 2—*Crude Barite (Domestic and Imported) Used in the United States*

SHORT TONS

In Manufacture of	1938	1939	1940	1941	1942	1943	1944	1945	1946	1947
Ground barite.....	193,728	192,112	200,899	243,846	200,443	225,154	360,045	482,442	465,468	561,230
Well drilling.....	126,697	125,560	138,055	154,760	117,380	144,452	277,792	407,871	372,610	467,350
Paint.....	8,227	9,750	11,056	31,009	18,484	15,000	23,000	21,000	26,000	29,000
Glass.....	7,963	12,586	12,697	22,615	21,895	25,464	24,153	25,761	29,181	33,641
Rubber.....	2,944	3,319	4,283	9,800	6,334	8,000	10,000	10,000	20,000	17,000
Other, including grinding loss...	47,897	40,897	34,808	25,562	36,350	32,238	25,100	17,810	17,677	2,974
Lithopone.....	117,007	141,556	136,885	153,982	144,821	129,493	134,597	139,228	154,166	167,321
Barium chemicals.....	54,250	58,015	66,604	93,005	104,160	99,097	100,921	99,173	102,439	107,267
Total.....	364,985	391,683	404,388	490,833	449,424	453,744	595,563	720,903	722,073	835,818

Oil-well Drilling Muds

In the rotary drilling of oil wells, a drilling bit is rotated by a hollow central shaft. A mud, pumped down this hollow shaft, removes the cuttings as they are formed and carries them up the annular space between the drill stem and the wall of the hole to the surface. In addition, this fluid or mud lubricates and cools the bit, seals off the wall of the hole and develops sufficient head to withhold abnormal pressures

encountered in the drilling. It is in the performance of this last function that barite is useful.

The oil fields in the Gulf Coast area, as well as those in lower California, have abnormally high pressures in the producing zones. When this pressure is greater than the hydrostatic head of the mud, the oil or gas will blow out of the well, frequently with disastrous results. These pressures are controlled by increasing the gravity of the drilling fluid by the addition of barite. Unweighted muds generally are clay-water mixtures and barite can be added to this mixture by adjustment of the clay content to produce a heavy but still pumpable mud fluid. Materials other than barite, chief of which is iron oxide, have been employed for this purpose successfully. However, because of the color of iron oxide, barite appears to be preferred by the drillers. Barite is inexpensive, has the necessary high specific gravity, is clean to handle and is generally free from harmful impurities. Consequently its use has increased markedly and it is employed in all parts of the world. Muds having a gravity as high as 2.5 can be prepared with barite, although such heavy muds are not always necessary.

Lithopone and Barium Chemicals

Because of the similarity in methods of production, lithopone and barium chemicals can be treated together. Both kinds of crude barite are roasted in a rotary kiln together with carbon at a temperature approximating 2400°F and the barium sulphate is reduced to barium sulphide. While barium sulphate is extremely insoluble in water, barium sulphide is quite soluble. The "black ash" or barium sulphide product is leached with water to yield a solution, which, owing to hydrolysis, is a solution of $\text{Ba}(\text{OH})_2$ and $\text{Ba}(\text{SH})_2$. Impurities and excess carbon are removed by filtering. The crude barite used for this operation should be as free as possible from impurities, since iron oxide, and to some extent alumina and silica, react with the barium sulphide in the course of the furnace operation, forming barium compounds that are generally insoluble. One per cent of iron oxide can render insoluble as much as 4 pct of barium sulphide, hence it is desirable to have the kiln-feed material as nearly pure as possible.

The barium solution prepared by leaching the "black ash" is used to precipitate lithopone and other barium chemicals. If the precipitant employed is a solution of zinc sulphate, the precipitate produced is a mixture of barium sulphate and zinc sulphide. When this precipitate is filtered, washed, dried and calcined under properly controlled conditions, quenched in water, wet-ground and subsequently dried, the product is lithopone. Although lithopone is only 70 pct barium sulphate, approximately one ton of crude barite is consumed for each ton of lithopone produced. The product is used as a pigment in paints and inks.

If the precipitant employed with the black-ash solution is sodium carbonate, the precipitate is barium carbonate. It may be filtered, washed, dried and distintegrated for use as barium carbonate. In addition, barium carbonate may be converted to other barium chemicals. If barium carbonate is heated with carbon, barium oxide is produced. This can be oxidized to barium peroxide or hydrated to barium hydroxide.

If the precipitant employed is sodium sulphate, the precipitate produced is barium sulphate or *blanc fixe*. This is filtered, washed, dried and employed as a filler in paints, inks, rubber, and other materials.

Barium nitrate and barium chloride usually are produced by the action of the corresponding acids on barium carbonate. Barium chloride may be electrolyzed in the fused state to produce barium metal.

Barium chemicals, in the order of their tonnage, are barium carbonate, *blanc fixe*, barium chloride, barium nitrate, barium oxide, barium hydroxide, and barium peroxide.

For Glass and as Filler

Barite crushed to pass 10 or 20-mesh is employed in the production of glass in continuous tanks. Its function is primarily one of fining or homogenizing the glass. Of the various glass-batch ingredients, the soda ash is the first to melt. The barite dissolves readily in the soda ash, increasing its density so that the liquid tends to drain toward the bottom of the batch. As the melting progresses and the temperature is increased, the dissolved barium sulphate subsequently reacts with silica, producing gaseous sulphur dioxide and oxygen. These gases rise from the bottom of the tank, stirring the glass and sweeping occluded gases from the melt. The glass has the appearance of boiling during this process. As the molten glass moves into the working end of the tank, which is somewhat cooler, the gassing ceases and any free sulphur dioxide and oxygen are resorbed by the glass. The presence of the small amount of barium oxide in the finished glass tends to increase the brilliance of the glass, in addition to improving its appearance by the process of homogenization.

Bleached ground barite has been used as an extender pigment in paint for some time. Originally it was employed as an adulterant for white-lead paint, on the basis of its high gravity. Its low index of refraction means that it contributes little to hiding power in a paint, but it does have low oil absorption and other desirable properties in the production of paints of many kinds. Other extender pigments have made serious inroads on the use of bleached barite in paints and inks. It is used also as a filler in oilcloth, linoleum, rubber, X-ray-proof plaster and concrete, brake linings and other materials.

PRICE HISTORY

Barite always has been and probably always will be a relatively low-priced material because of its abundance and wide distribution throughout the earth's crust. There are so many deposits that those to be worked can be selected with regard to ease of mining, concentrating and shipping. In many of its uses, barite is in direct competition with other low-priced materials and for many of its uses it is not indispensable. Prices at the point of production are governed largely by the cost of transportation to the marketing centers. The fact that freight frequently consumes a large portion of the delivered price has influenced strongly the location of the deposits worked. This is particularly true of the Arkansas deposit, which is the nearest to the Gulf Coast oil fields. This has been reflected in a rapid increase in production in that area. Table 3 shows the price of crude barite f.o.b. mines. The upward trend in price from 1933 reflects somewhat the rise in labor costs generally encountered in the producing areas.

TABLE 3—Average Price of Crude Barite in Missouri 1929–1947 per Short Ton

Year	Price	Year	Price	Year	Price
1929.....	\$7.42	1936.....	\$6.27	1942.....	\$6.44
1930.....	7.08	1937.....	7.22	1943.....	7.20
1931.....	5.77	1938.....	7.36	1944.....	7.44
1932.....	5.42	1939.....	6.78	1945.....	7.68
1933.....	4.54	1940.....	6.78	1946.....	7.23
1934.....	4.90	1941.....	6.30	1947.....	7.39
1935.....	5.52				

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CHAPTER 4

BAUXITE*

By E. C. HARDER†

BAUXITE is known mainly as the ore from which aluminum is smelted but it has large use also in the manufacture of artificial abrasives and as a basis for certain chemical industries. A small amount is used for refractories and for other purposes.

COMPOSITION

Dana and others give the mineral formula of bauxite as $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ and the composition as Al_2O_3 , 73.9 pct; H_2O , 26.1 pct. It has been definitely shown, however, that bauxite does not exist as a specific mineral but rather as a rock. The term is now used synonymously with aluminum ore and it embraces gibbsite (hydrargillite or alpha trihydrate), $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (Al_2O_3 , 65.4 pct; H_2O , 34.6 pct); boehmite (alpha monohydrate), $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (Al_2O_3 , 85 pct; H_2O , 15 pct); diasporé (beta monohydrate), $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (Al_2O_3 , 85 pct; H_2O , 15 pct), and mixtures in various proportions of any two of them. Bauxite of the Mesozoic and Cenozoic in Europe is predominantly a mixture of gibbsite and boehmite, subordinately a mixture of boehmite and diasporé, or gibbsite and diasporé. The bauxite of North and South America, tropical Africa, Asia, and Australasia consists largely of gibbsite. Corundum (Al_2O_3) is not included under bauxite, although gradations from bauxite to emery or corundum exist.

All bauxite, irrespective of the aluminum minerals composing it, contains certain impurities, including silica, in the form of clay minerals (kaolinite, halloysite, and others) or quartz, iron oxide (as hematite or goethite), titania (as leucoxene or rutile), iron sulphide (as pyrite or marcasite), iron carbonate (siderite), and calcium carbonate (as calcite); the last three mentioned in minor amount and of local occurrence only. Bauxite belongs to a group of partly consolidated materials called laterites, formed by surface weathering. This group includes also impure siliceous and ferruginous bauxite and siliceous and

* Through the courtesy of the McGraw-Hill Book Co., much of the material herein was abstracted from the chapter on Ores of Aluminum, by E. C. Harder, in *The Aluminum Industry*, by J. D. Edwards, F. C. Frary and Z. Jeffries, New York, 1930. Other references are given in the bibliography at the end of this chapter.

† Vice President, Aluminium Secretariat Limited, Montreal, P.Q., Canada.

aluminous iron ores and manganese ores. Phosphatic bauxite occurs in a few places.

PROPERTIES

Gibbsite is white or light shades of gray, cream or pink. Its hardness is 2.5 to 3.5; specific gravity, 2.3 to 2.4; crystal system, monoclinic, crystals tabular parallel to 001, often fibrous, concretionary, stalactitic; luster, vitreous to pearly; generally translucent; cleavage, parallel to 001; disassociation temperature, approximately 300°C.

Boehmite, a new mineral described by J. Boehm in 1925, confirmed and named by J. de Lapparent in 1930, has some properties not yet definitely determined. It occurs in grayish, brownish and reddish shades. Its hardness is between that of gibbsite and diasporé; specific gravity, 3.01 to 3.06 (artif.); crystal system, orthorhombic, crystals lenticular tabular, best developed along 110 and 001; angle between the faces *m* near 63°; cleavage, parallel to 010; X-ray pattern distinctly different from that of diasporé.

Diasporé is white or light shades of gray or brown. Its hardness is 6.5 to 7; specific gravity, 3.3 to 3.5; crystal system, orthorhombic, crystals prismatic, flattened, parallel to 010; luster, pearly to vitreous; transparent to translucent; birefringence high; cleavage, parallel to 010; disassociation temperature, approximately 500°C.

Bauxite as it occurs in nature rarely exhibits the distinct characteristics of its constituent minerals. These become apparent only in examination of thin section under the microscope, by the determination of heating curves, by chemical analysis or by X-ray tests. Not all the constituents in bauxite are recognizable even by such methods and it is believed therefore that much of the alumina is present in the form of colloidal hydrogels, with a variable combined water content. Bauxite is a medium soft to hard rock, has a cellular, porous or fine-grained compact structure, a conchoidal or uneven fracture, and ranges in color from light gray, cream, pink or yellow to dark brown and dark red. In many localities the bauxite is characterized by an oölitic or pisolitic texture, the oölites ranging in size from less than $\frac{1}{20}$ in. to $\frac{1}{2}$ in. or more. The oölites may have a concentric texture or they may be homogeneous. Small oölites may occur grouped together within larger ones. The color of the oölites generally differs somewhat from that of the matrix—usually, but not always, being darker. There is much bauxite that does not show oölitic texture but has an even-grained, homogeneous or claylike appearance, dense, porous or cellular. In many places oölitic and nonoölitic bauxite occur together in the same deposit.

MODE OF OCCURRENCE

Bauxite deposits occur in a number of different geologic associations but most of them can be grouped into four main classes:

1. Blanket deposits occurring at or near the surface in horizontal, tilted, or undulating sheets and lenses.
2. Beds and lenslike deposits occurring at definite stratigraphic horizons interlayered with sediments or between sediments and igneous rocks.
3. Pocket deposits or irregular masses enclosed within limestone or clay or igneous rock.
4. Detrital deposits formed by the mechanical breaking up, transportation and redeposition of the material from deposits of the other three types.

These four types of deposits are closely related to each other and are in many cases gradational. There is a strong possibility that the first three have a somewhat similar origin. Table 1 shows the general age relations of the principal bauxite deposits of the world.

Blanket Deposits—Horizontal blanket deposits of bauxite or laterite are commonly found in tropical or semitropical regions, where they occur on base-leveled surfaces. Some of them are at low elevations and others occur as cappings on extensive plateaus or on flat-topped hills representing outliers or remnants of such plateaus. The elevated bauxite-bearing plateaus are former base-leveled surfaces that have been raised and subjected to erosion subsequent to the original peneplanation and formation of bauxite. In many places the laterite or bauxite deposits are at the surface, covered only by sparse vegetation; elsewhere, varying thicknesses of soil cover them. Generally the surface and upper portion of the deposits is hard and indurated, owing to infiltration and cementation by iron oxide or siliceous material. With depth, it becomes softer and at the bottom it passes rather abruptly into the underlying residual clay. Locally small, irregular pipes or networks of pipes of bauxite project downward into the residual clay from the lower surface of the bauxite layer.

Blanket deposits of bauxite or laterite range in thickness from less than 1 ft to 75 ft or more; the average is from perhaps 5 to 25 ft. Horizontally blanket deposits may extend for a few hundred feet or for several miles. The entire layer, except for variations at the immediate surface or at the base, may be fairly uniform and may consist of high-grade bauxite or of siliceous or ferruginous bauxite. On the other hand, there may be variations both vertically and horizontally, with the different phases lying in well-marked layers or grading into each other laterally or being irregularly intermixed.

TABLE 1—*General Age Relations of Principal Bauxite Deposits*

Cenozoic	
Pleistocene and Recent	Tropical lateritic bauxite of Brazil, French West Africa, Gold Coast, Nyasaland, Malaya, Netherlands Indies, Caroline Islands, Australia
Pliocene	Oregon laterite German bauxite (Vogelsberg Mountains) Jamaica, Haiti and Santo Domingo bauxite—underlain by Oligocene
Miocene	Guiana bauxite
Oligocene	Australian bauxite (Victoria) Irish bauxite (County Antrim)
Eocene	Indian bauxite and laterite
Upper	
Middle	
Lower	United States bauxite—underlain by Lower Eocene or Lower Cretaceous Dalmatian bauxite—underlain by Lower Eocene and Upper Cretaceous Montenegrin bauxite (Bar and Ulcinj)—underlain by Upper Cretaceous Istrian bauxite—underlain by Upper Cretaceous Spanish bauxite—underlain by Eocene and Rhaetic Kashmir deposits (Jammu)—underlain by Jurassic Hungarian bauxite—underlain by Rhaetic
Mesozoic	
Cretaceous	
Upper	
Danian	
Senonian	Greek bauxite—underlain by Jurassic French bauxite (Herauld)—underlain by Jurassic
Middle	
Turonian	
Cenomanian	
Albian	Italian bauxite (Central Apennines) Montenegrin bauxite (Kotor and Niksic)—underlain by Lower Cretaceous French bauxite (Var)—underlain by Urgonian, Neocomian and locally Jurassic
Lower	
Aptian	
Urgonian	French bauxite (Ariege)—underlain by Jurassic
Neocomian	Rumanian bauxite (Bihar)—underlain by Malm
Jurassic	
Upper (Malm)	
Middle (Dogger)	
Lower (Lias)	
Triassic	
Upper	
Rhaetic	Croatian bauxite—underlain by Middle Triassic
Keuper	
Middle	
Lower	Chinese diaspore (Poshan)—underlain by "Permo-Carboniferous"
Paleozoic	
Permian	
Upper Carboniferous (Pennsylvanian)	Missouri diaspore—underlain by Pennsylvanian Pennsylvania diaspore—underlain by basal Pennsylvanian
Lower Carboniferous (Mississippian)	Chinese boehmite (Yunnan)—underlain by Devonian Russian bauxite (Tikhvin)—underlain by Devonian
Devonian	Chinese diaspore (Kweichow)—underlain by Ordovician Russian bauxite (Ural)—in Middle and Lower Devonian

Interlayered Deposits—Most layers and lenses of bauxite or laterite interbedded with sediments or lying between sediments and igneous rocks are what might be termed “fossil blanket deposits.” They represent surface deposits of past geologic ages that have been submerged subsequent to their formation and have had deposited upon them successive beds of later sediments. As far as texture and composition are concerned, interbedded bauxite deposits in general resemble surface deposits, except that they have a tendency to be harder, more compact and more indurated, owing, no doubt, to the weight of the overlying sediments. They show the same variations in grade, however, and have the same impurities. The overlying rocks may be limestone, shale or sandstone; the underlying rocks may be igneous or sedimentary. In many places rocks with which the bauxite layers and lenses are interstratified have suffered deformation, with resultant folding and faulting of the bauxite layers. In places where the deformation has been pronounced, as in parts of France, Rumania and Greece, the partial alteration of gibbsite or boehmite to diasporite has been noted. Where the deformation has been extreme, as in some of the Aegean Islands, corundum (emery) has developed.

Pocket Deposits—Pocket deposits occur in many places associated with interbedded bauxite layers and lenses. They represent irregularities in the surface upon which the bauxite was formed. In many places bauxite pockets are directly connected with bauxite layers or lenses as extensions from their lower surfaces into pre-existing depressions on the upper surface of the stratigraphically underlying rock, commonly limestone or igneous rock but in places clay. Elsewhere, pockets are scattered irregularly or occur in groups unconnected with bauxite layers or lenses, which, if they ever existed, have been removed by erosion.

The pocket deposits of bauxite in many places show sharp contacts with the enclosing limestone, igneous rock or clay, while elsewhere cushions or gradational margins of kaolin or of bauxitic clay high in alumina occur. Bauxite pockets in limestone may be directly in contact with the limestone or may be separated from it by masses of residual earth, such as terra rossa, derived from limestone decay. The shape of the pockets is irregular; some are approximately equidimensional but most are irregularly pod-shaped. The manner in which they cut across the bedding of the enclosing rocks, and their arrangement in groups, suggests deposition of the protore as fillings of solution caverns.

Detrital Deposits—Detrital bauxite deposits originate from other pre-existing bauxite deposits and may be talus accumulations, stream gravels or sands, or more or less consolidated low-level surface layers.

ORIGIN

The hypotheses that have been advanced to explain the origin of bauxite may be grouped under four main headings: (1) chemical sedimentation, (2) chemical replacement, (3) weathering in situ, (4) detrital deposition.

Many geologists have considered it necessary to explain the formation of bauxite deposits by processes of solution and redeposition. Igneous rocks and clays are looked upon as the source of the aluminum. As solvents, various acids, alkalies and salts were taken into consideration—for instance, nitric acid, derived from bacterial activity, or from lightning discharges; sulphuric acid resulting from the decomposition of sulphides; sodium chloride from marine waters, and sodium hydroxide or sodium carbonate obtained by decomposition of various rocks. Hot springs are called upon as agents. Deposition is believed to occur in enclosed basins by reaction with carbon dioxide, organic acids, hydrogen sulphide or calcareous waters, with accompanying cooling.

Some geologists have visualized the formation of certain bauxite deposits at depth through replacement of limestone or other rocks by aluminum-bearing solutions.

In recent years the role of weathering processes in the formation of bauxite and laterite has been clearly recognized, and the general opinion today is that most bauxite deposits, rather than being the result of solution and redeposition of aluminum, are residual products resulting from the intensive weathering of aluminum-bearing rocks, involving the solution and removal of constituents other than aluminum. This process is called lateritization and the original rocks most commonly involved are syenite, granite, diorite, basalt, dolerite, crystalline schists, limestone, shale, and clay.

Certain bauxite deposits of minor importance are believed to be of detrital origin, being the result of mechanical concentration of bauxite fragments and particles from previously existing bauxite materials and in places their partial consolidation by infiltration of cementing substances.

DISTRIBUTION OF DEPOSITS

Although bauxite deposits occur abundantly in many parts of the world, the mining of bauxite in important quantities is confined to relatively few countries. Roughly, in the order of their importance during recent years, the principal bauxite-producing countries are United States, British Guiana, Surinam, France, Hungary, Russia, Netherlands Indies, Yugoslavia, Gold Coast, and Italy. Minor quantities of bauxite have been produced in Brazil, Greece, India, Malaya, Northern Ireland, Germany, Caroline Islands, Rumania, Spain, and Australia.

Principal Producing Countries

United States—Bauxite was first discovered in the United States near Rome, Georgia, in 1883. The first production occurred in Georgia in 1889 and in Arkansas 10 years later. Deposits occur in Arkansas, Georgia, Alabama, Tennessee, and Mississippi. The Arkansas deposits have furnished more than 90 pct of all the bauxite produced in the United States. They are alterations of nepheline syenite and clay and are overlain by Eocene clays and lignites. The deposits in northern Georgia, northern Alabama, and Tennessee occur as pockets in clays; those in southern Georgia and southern Alabama are in the form of beds and lenses interlayered between Eocene sediments.

The bauxites of the United States differ from those occurring in Europe in that usually they contain a relatively small amount of iron oxide and carry a high content of combined water. On an average they contain 56 to 59 pct Al_2O_3 , from less than 2 to about 6 pct Fe_2O_3 , from 5 to 8 pct SiO_2 and approximately 29 to 31 pct combined water. In general, the deposits in Georgia, Alabama, and Tennessee are lower in iron oxide and higher in silica than those in Arkansas. The bauxite deposits of Mississippi are of low grade and under present conditions are considered uncommercial.

There occur also in the United States, in central Missouri and in west central Pennsylvania, small and scattered deposits of diaspore, which have furnished a fairly regular production, mainly used in the manufacture of aluminous refractories. The deposits form small, irregular masses associated with burly or nodule clay in flint-clay pockets and lenses. They range in alumina content from 50 pct to more than 70 pct, depending on the amount of intermixed clayey materials.

British Guiana—Bauxite was first exploited in British Guiana in 1914 and shipments began in 1917. The principal deposits are in the Demerara, Ituni and Berbice River regions, from 65 to 125 miles south and southeast of Georgetown. They occur as horizontal or slightly tilted beds and lenses, in places outcropping along the rivers and small creeks and elsewhere overlain by a varying thickness of unconsolidated littoral sediments. In the presently exploited areas, this overburden of sand and clay ranges up to 100 ft or more in thickness and overlies 15 to 25 ft of bauxite. British Guiana bauxite contains 59 to 61 pct Al_2O_3 , 1 to 2.5 pct Fe_2O_3 , 2.5 to 4 pct SiO_2 , 2 to 3 pct TiO_2 and 30 to 32 pct combined water. It is used mainly for manufacture of aluminum but substantial quantities are also utilized in the manufacture of abrasives, chemicals and refractories. Most of it is exported to Canada and the United States but fairly large tonnages have been shipped also to the United Kingdom and continental Europe.

Surinam—Bauxite was discovered in Surinam about 1915 and the first shipments were made in 1922. Most of the ore is exported to the United States for manufacture of aluminum. It is found along Surinam, Cottica and Coermotibo Rivers, south and southeast of Paramaribo, and about 15 to 25 miles inland from the coast. It is of the tropical lateritic variety and occurs mostly as surface deposits, forming low hills and ridges in the coastal lowlands with only a few feet of soil overburden. The Surinam bauxite is of high grade, containing 55 to 57 pct Al_2O_3 , 8 to 12 pct Fe_2O_3 , 2 to 3 pct SiO_2 and 30 to 31 pct combined water.

France—The principal bauxite deposits of France occur in the departments of Var and Herault; minor deposits are in the departments of Bouches du Rhone and Ariege. About four fifths of the bauxite produced in France has come from the Var district, and three fourths of the remainder from Herault. Besides furnishing the total requirements of France, these deposits have supplied a considerable portion of the bauxite used elsewhere in Europe, particularly in the United Kingdom and Germany. Bauxite was discovered in France in 1821, near Les Baux, in Bouches du Rhone, from which locality it receives its name. The first recorded production occurred there in 1873.

The French bauxite is mostly of the dark red, high-iron type. This variety ordinarily contains 56 to 59 pct Al_2O_3 , 20 to 25 pct Fe_2O_3 , 2 to 5 pct SiO_2 and 2.50 to 3.50 pct TiO_2 . Small amounts of white and gray bauxite are produced, the former containing 60 to 70 pct Al_2O_3 , about 4 to 12 pct Fe_2O_3 and 8 to 16 pct SiO_2 and the latter having a variable composition ranging between the red and the white bauxite. All three types contain 12 to 14 pct combined water. The different varieties all occur in association with limestone as pockets or interlayered beds and lenses. They vary in relative abundance in the different districts.

Hungary—The Hungarian bauxite deposits occur in an area north of Lake Balaton and extend thence northeastward toward Budapest. Most of the ore produced thus far has come from the Vertes Mountains, in the northeastern part of the belt, but bauxite is mined in the Bakony region also, in the western part of the belt. The bauxite ranges from yellow to brown and red in color and that of commercial grade contains 57 to 60 pct Al_2O_3 , 12 to 20 pct Fe_2O_3 , 2 to 7 pct SiO_2 and 14 to 16 pct combined water. However, a large proportion of the material in the deposits is of low grade and must be removed along with the commercial ore, increasing the mining expense. The Hungarian bauxite is similar to that of the Mediterranean region in being associated with limestone in pockets and lenses. It was first exploited in 1925 and since that time has furnished a large proportion of the bauxite used in Europe for manufacture of aluminum.

Russia—The development of Russian bauxite deposits began about 20 years ago with the inauguration of the first Five-year Plan. At first mining was confined to the Tikhvin district, southeast of Leningrad, the bauxite being shipped to refining plants connected with aluminum smelters at Volkhov, near Leningrad and on the Dnieper River. Intensive geological research subsequently disclosed large bauxite deposits in the northern and central Urals and during the past 10 years or more these have been the main source of raw material for the Ural refining plants and smelters. The Tikhvin bauxite is of low and variable grade, containing 35 to 54 pct Al_2O_3 , 15 to 20 pct Fe_2O_3 , 10 to 20 pct SiO_2 , and 10 to 20 pct combined water. The bauxite from the Ural deposits is reported to be of better quality, at least in part.

Netherlands Indies—Bauxite was first mined in the Riouw Islands, near Singapore, in 1935, but production increased rapidly because of the requirements of the Japanese aluminum industry. Substantial shipments have been made to Germany and occasional cargoes to North America. The bauxite from the Riouw Islands contains approximately 54 pct Al_2O_3 , 2 pct SiO_2 , 14 pct Fe_2O_3 , 1 pct TiO_2 and 29 pct combined water.

Yugoslavia—Bauxite occurs in Yugoslavia mainly in the Istrian Peninsula, south and southeast of Trieste, and in Dalmatia, Herzegovina and Montenegro. The Istrian bauxite field, formerly in Italy, was awarded to Yugoslavia as a result of World War II and is by far the most important of the Yugoslav bauxite districts, covering a considerable part of the peninsula. A small portion remains in the Free Territory of Trieste. Both Istrian and Dalmatian bauxite were first mined during World War I on a small scale and mining has been more or less continuous for the past 30 years or so. The Dalmatian bauxite has originated mainly from the Drnis and Sinj districts and from certain islands along the Adriatic coast but there are also large deposits of bauxite in the Obrovac district, which, because of their low grade, have not been extensively exploited. The deposits of Herzegovina were opened up shortly before World War II and most of the production thus far has come from the region west and northwest of Mostar.

The Istrian bauxite is of high grade, most of it being found in the form of pockets, abundant and widely scattered in the surface of limestone. It is of two main types; one dark red and similar to that produced in southern France and the other a yellowish variegated bauxite. The former generally contains between 55 and 58 pct Al_2O_3 , 22 and 25 pct Fe_2O_3 , 2 and 4 pct SiO_2 and 12 and 14 pct combined water. The latter commonly carries 60 to 65 pct Al_2O_3 , 10 to 15 pct Fe_2O_3 , 5 to 9 pct SiO_2 and 12 to 14 pct combined water. The two varieties may occur together in the same deposit or they may form separate deposits.

The Dalmatian and Herzegovinan deposits are of variable quality and many of them occur as tilted beds and lenses requiring extensive underground operations. They contain approximately 50 to 54 pct Al_2O_3 , 20 to 24 pct Fe_2O_3 , 1 to 3 pct SiO_2 and 18 to 22 pct combined water. The Montenegrin deposits are mostly of low grade and have not been commercially exploited.

Gold Coast—Bauxite deposits of the lateritic type occur in the Gold Coast in the northern part of the Gold Coast Colony and the southern part of Ashanti, as lenses in a predominantly ferruginous laterite that forms cappings on flat-topped hills rising 1000 ft or more above surrounding lowlands. The cappings may have a thickness of 80 ft or more and the included bauxite lenses may range up to 50 ft thick. The Al_2O_3 content of the bauxite may vary from an arbitrarily specified lower limit for commercial ore to as high as 60 pct and, similarly, the Fe_2O_3 content may range from more than 25 pct downward to 4 or 5 pct; SiO_2 averages 2 or 3 pct; TiO_2 , 2 or 3 pct, and combined water 25 to 29 pct. Mining of Gold Coast bauxite was started in the Sefwi-Bekwai district in 1941, the bauxite being hauled by truck to the Kumasi-Takoradi line of the Gold Coast Railways during the first few years and then by a newly constructed branch railway connecting with this line at Dunkwa. Some bauxite was also mined during World War II at Mt. Ejuanema, situated along the Kumasi-Accra section of the Gold Coast Railways.

Italy—As a result of World War II, Italy ceased to be an important bauxite-mining country, owing to the forfeiture to Yugoslavia of the bauxite deposits on the Istrian Peninsula. Italy's only remaining producing mines are those in the Gargano and Spinazzoli areas in Apulia and these yield only a small production. A few deposits occur north of Naples and some low-grade occurrences are found in isolated districts in the central Apennines.

Minor Producing Countries and Important Potential Sources

Brazil—A small amount of bauxite was mined in Minas Gerais, Brazil, before World War II for local consumption and for export to Argentina. During the war, considerable tonnages were shipped to the United States and the United Kingdom but since then production has reverted to the prewar scale.

Greece—Greece has shown a moderate annual production of bauxite since about 1935 from mines in the Parnassus and Athens districts and on Amorgas Island in the Aegean. Disrupted conditions toward the end of World War II and subsequently have caused a stoppage of operations. Greek bauxite, although somewhat hard and refractory, is of good grade, containing about 56 to 59 pct Al_2O_3 , 16 to 20 pct Fe_2O_3 , 3 to 7 pct SiO_2 and 13 to 15 pct combined water.

India—Bauxite has been mined in India in small quantities for many years for local use in the chemical and refractories industries; latterly, it has been mined for shipment to Japan also. During the war, Indian bauxite was shipped to the United Kingdom. Recently alumina-refining plants and aluminum smelters were established in India and it may be expected that bauxite production will increase. Indian bauxite has the following average range in composition: Al_2O_3 , 54 to 58 pct; Fe_2O_3 , 3 to 8 pct; SiO_2 , 1 to 3 pct; TiO_2 , 6 to 11 pct; combined water, 26 to 29 pct.

Malaya—Bauxite mines were operated by Japanese interests in Malaya for some years prior to World War II and during the war considerable tonnages were shipped to Japan. Shipments have ceased entirely since the end of the Japanese occupation.

Northern Ireland—Substantial tonnages of low-grade bauxite were mined in Northern Ireland during World War II because of difficulties in obtaining bauxite from overseas. Since the war, mining operations have been greatly reduced.

Other Countries—A number of countries possess bauxite deposits that have not been exploited because of their low grade, small size, difficulties of development or remoteness from bauxite markets. Worthy of special mention in this category are the recently discovered bauxite deposits of Jamaica, Haiti and the Dominican Republic. Although of low grade compared with presently used commercial bauxites, these are conveniently situated with respect to aluminum-ore markets and probably are adaptable to low-cost mining, which may in part compensate for the greater expense in processing. The Jamaican bauxite deposits occur in the limestone highlands in the north central and west central parts of the island and occupy depressions on the uneven erosion surface of the limestone. They extend directly from the limestone floor almost to the surface, being covered by only a foot or so of sod and soil. The ore is soft and earthy and yellowish brown to dark red in color. Its average composition is as follows: Al_2O_3 , 46 to 50 pct; Fe_2O_3 , 16 to 20 pct; SiO_2 , 1 to 2 pct; TiO_2 , 2 to 3 pct; P_2O_5 , CaO , etc., 1 to 3 pct; combined H_2O , 26 to 29 pct.

Also of future importance are the lateritic bauxites of French Guinea, West Africa. Of these the deposits on Los Islands near Conakry, which are now in process of development, are most accessible but large areas of low-grade bauxite and laterite are also found in the Boke and Tougue districts in northern and central French Guinea, respectively. The Los Islands bauxite lies as a decomposition blanket of varying thickness on the surface of nepheline syenite and generally is overlain by several feet of soil and laterite, which also occur mixed with the ore itself. The approximate range in composition is: Al_2O_3 , 50 to 55 pct; Fe_2O_3 , 12 to 14 pct; SiO_2 , 4 to 7 pct; TiO_2 , 1.5 to 2.5 pct; combined H_2O ,

25 to 28 pct. Little is known as yet of the interior deposits in French Guinea, except that they represent local concentrations of high-alumina material in extensive areas of ferruginous laterite.

The bauxite deposits of Rumania have been mined on a small scale when emergency supplies were required, but normally it is uneconomical to operate them. They are similar to those of Greece in physical and chemical characteristics. The bauxite deposits of Germany and Spain are small and relatively unimportant. There are large deposits of bauxite in Nyasaland, but their location is unfavorable and the bauxite itself is a low-grade quartzose material. Several states in Australia, including Queensland, New South Wales, Western Australia, and Tasmania, have numerous deposits of laterite and low-grade bauxite. Some deposits of a fairly good grade of bauxite in Victoria have yielded a small annual production. During the war years, moderate amounts of bauxite were produced in the Japanese-mandated Caroline Islands, most of it originating in Palau. The ore appears to be similar to that occurring in Malaya and Netherlands Indies. Small amounts of bauxite are reported to have been produced in Indo-China from deposits said to occur in the region northwest of Hanoi. China has large deposits of low-grade siliceous diaspore and diasporic clay in Manchuria, Shantung, Kweichow and Yunnan, in the latter associated with boehmite. Relatively small amounts have been produced for refractory purposes and for some of the Japanese-operated aluminum-producing plants.

POLITICAL AND COMMERCIAL CONTROL

Like those of most mineral raw materials, bauxite supplies are unequally distributed among the important world powers, particularly from the viewpoint of the aluminum industry in these powers.

The United States, as the leading producer in the world of metallic aluminum and aluminum chemicals, is insufficiently supplied with bauxite reserves. Although the deposits in the United States still furnish an important production, a large tonnage of bauxite is annually imported—mainly from Surinam, subordinately from British Guiana—and little is exported, except in the form of refined products. The import duty on bauxite into the United States has been reduced recently from \$1 per ton to 50¢ per ton.

Canada, the second largest producer of aluminum and the world's largest producer of crude aluminium abrasives, has no bauxite deposits within its borders. Imported bauxite is obtained for the most part from British Guiana but smaller amounts are imported from the United States and Surinam and, occasionally, elsewhere.

Germany, before World War II, was the world's second largest producer of metallic aluminum and aluminum products. It had almost no commercial bauxite and obtained its requirements mainly from

Hungary and subordinately from France, Italy, and Yugoslavia. Germany's position as a future producer of aluminum is uncertain.

France is well supplied with bauxite reserves, not only in the metropolitan area but also in the French African colonies. It may rely on its own deposits to furnish the requirements of the domestic aluminum and other bauxite-consuming industries, as well as to supply substantial exports for many years to come. France imports little or no bauxite from abroad, but has exported large quantities to the United Kingdom, Germany, and elsewhere.

The aluminum industry in the United Kingdom has in the past been supplied with bauxite mainly from France, but recently to an increasing extent from the British colonies such as Gold Coast and British Guiana. Bauxite deposits are found in many of the British dominions and colonies, notably India, Australia, Malaya, Nyasaland, Gold Coast, British Guiana, and Jamaica. Some of these countries are supplying large quantities to the world's bauxite markets; others have bauxite deposits of great potential importance, while still others have low-grade deposits of little or no present interest.

Norway and Sweden, with their important aluminum industries, are dependent entirely upon imported bauxite. In the past, bauxite supplies have been obtained mainly from France, Italy, and Greece, but it is conceivable that in the not distant future Scandinavian aluminum producers may go farther afield for their requirements.

Switzerland, an important producer of aluminum, has no bauxite deposits. Raw material for its plants has been obtained largely from France in the form of alumina manufactured from French bauxite.

Italy lost its large Istrian bauxite reserves as a result of World War II and in the future will be mainly dependent upon imported bauxite to supply its aluminum plants and other bauxite-consuming industries. France and Yugoslavia may be called upon to furnish these requirements.

Hungary produced aluminum, aluminous cement and aluminum chemicals in small amounts prior to World War II and during the war the aluminum industry was considerably expanded. It has large bauxite reserves, which, before the war, supplied the German aluminum industry; perhaps they will now similarly supply the Russian aluminum industry.

The Russian aluminum industry expanded rapidly prior to and during the war years. Fairly extensive but low-grade deposits of bauxite were discovered, first near Leningrad and subsequently in the Urals, and developed concurrently with the aluminum industry. Up to the present little or no foreign bauxite has been used in Russian bauxite-consuming plants but it is possible that in the future Russia may change its policy and become an importer of high-grade bauxite from neighbor-

ing countries such as Rumania, Hungary, and Yugoslavia, instead of using exclusively domestic low-grade ore.

Yugoslavia, by the acquisition and nationalization of the large Istrian reserves, has greatly increased in importance as a bauxite nation. At present it has only one or two small bauxite-consuming plants but, with large ore reserves available, it is ambitious to develop a domestic aluminum industry.

Japan, like Germany, had a large and expanding aluminum industry prior to World War II. Bauxite from Netherlands Indies and Malaya was the raw material used in most of the large plants but some of the smaller ones used also Korean alunite, Manchurian clays, and occasionally European and Indian bauxite. The future of the Japanese aluminum industry is uncertain.

A number of countries possess important bauxite deposits but have no aluminum or other important bauxite-consuming industries. Thus, the Netherlands has no aluminum smelters but has large bauxite deposits in Surinam and in the Netherlands Indies, the former furnishing an important part of the United States requirements and the latter in the past having supplied Japan.

Brazil also has large bauxite deposits but at present has only negligible bauxite-consuming industries.

PRODUCTION AND CONSUMPTION

Although bauxite was discovered in France in 1821, there is no record of any production until 1873, when 200 tons was mined. At the end of the century the output had not reached 50,000 tons. Thereafter, however, bauxite mining progressed rapidly and in 1913 more than 300,000 tons was produced. In the United States, the first bauxite production dates from 1889, when 728 tons was mined in the Rome district, Georgia. The Arkansas bauxite mines began producing in 1899, with an output of 5045 tons in that year. Until World War I started, more than 95 pct of the bauxite produced annually came from the mines of France and the United States. During the war, however, the necessity for the opening up of new bauxite deposits became apparent and while the deposits of Istria and Dalmatia were being developed by the Central Powers the Allies turned their attention to the newly discovered deposits of British Guiana and Surinam. The British Guiana mines started shipments in 1917 and the Surinam mines in 1922. Somewhat later, bauxite was discovered in Hungary and was developed for the benefit of the German aluminum plants. Bauxite production began in Russia in the late twenties. During the past 15 years it has continued at a high and increasing rate.

Fig 1 shows graphically the bauxite production from 1935 to 1946 in the principal producing countries.

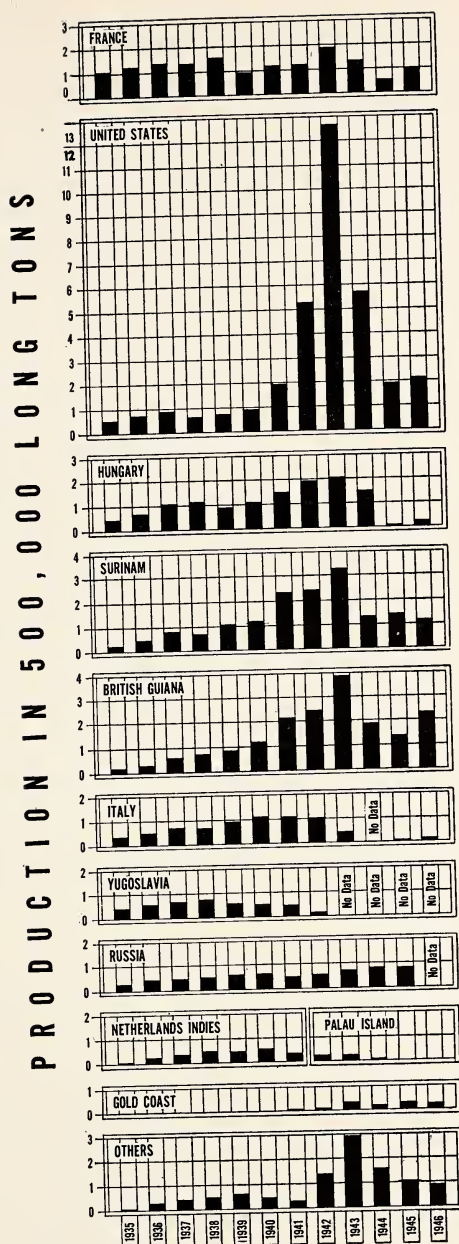


FIG 1—BAUXITE PRODUCTION IN PRINCIPAL PRODUCING COUNTRIES, 1935–1945.
From Minerals Yearbook, Bureau of Mines.

PROSPECTING AND EXPLORATION

Although bauxite deposits were formed under conditions existing in warm climates, they are not necessarily confined to tropical or subtropical regions, owing to variations in climatic conditions in past geologic times. Thus the Arkansas bauxite deposits occur at latitude 35°N , those of southern Europe between 40° and 50°N and those of the Tikhvin region in Russia at latitude 60°N . Bauxite deposits usually are discovered from outcrops and fragments of float. Rock associations, however, may serve as a guide, bauxite being commonly found with clay, limestone or certain igneous rocks such as syenites, feldspathic schists, dolerites and basalts. Probably the most striking association of bauxite is with old land surfaces. Thus bauxite deposits in the older rocks occur along unconformities representing long time intervals, while those of recent origin occur on moderately level, peneplained surfaces that have been undisturbed for a long period of time.

Once found by outcrops, bauxite deposits are explored by drilling. It is generally preferable to use hand drills, as most bauxite deposits occur in remote regions where transportation is difficult; moreover, many deposits are found at relatively shallow depths. In places, however, as on the flanks of the ore bodies or elsewhere where they are deeply buried, power drills have been used successfully, although coring generally has been found unsatisfactory. It is best to perform the exploration by drills in two stages, the early drilling, widely spaced, and merely for the purpose of determining the quality and estimating approximate tonnages; the later drilling at close intervals to serve as a guide to mining. A few test pits should be sunk on all deposits to supplement the drilling, mainly with the object of securing samples for washing and other beneficiation tests.

MINING METHODS

The methods used in mining bauxite differ somewhat in different countries and with different types of deposits. In deposits occurring in the form of extensive surface blankets or in beds and lenses interlayered with unconsolidated sediments, such as are being mined in Arkansas and in northern South America, quarrying is a common method of mining. The overburden, where present, is removed by hand or by scrapers or, where thick, by power shovels or draglines, and the upper surface of the bauxite layer is thoroughly cleaned by means of picks and shovels. Holes for blasting are then drilled into the ore bed vertically, starting at the surface and penetrating into the lower portion of the bauxite layer. Generally such holes are drilled in series parallel to the existing quarry faces. After blasting, the broken bauxite is picked up by power shovels, loaded on mine cars, and transported by rail to beneficiation plants.

Where the overburden is too deep to be removed by stripping or where lenses and layers of bauxite are interlayered with solid rock, as limestone is in the European fields, and the attitude of the enclosing rock is such that the deposits reach considerable depths, quarrying methods are used along the outcrops and underground mining methods at depths. The underground mining is advanced by a series of drifts and crosscuts and caving is employed in retreating. The bauxite is removed from the workings in mine cars, through tunnels, shafts or inclined planes, according to the form of the deposit and the method of working, and is transported from the mines to railway stations or seaports by motor lorries. European bauxite is not subjected to beneficiation.

Pocket deposits of bauxite, such as occur enclosed in limestone at various places in southern Europe and in clay in southeastern United States, are mined by open quarrying methods. Bauxite pockets usually are of limited extent and the mining is mainly by hand with the use of picks, shovels, and wheelbarrows. In large pockets, mine cars may be used. The bauxite is raised from the open pits along inclines or by elevators and transported to railway stations by motor lorries. At several localities in Europe where the conditions permit, aerial cableways are in use between mines and loading stations.

PREPARATION FOR MARKET

In Arkansas, British Guiana, Surinam and the Netherlands Indies, the bauxite is beneficiated before marketing. In Europe, the bauxite is shipped direct to consuming plants in the crude state as mined. In the United States and in the Guianas the crude bauxite, as mined, consists of fines and fragments ranging in size up to a foot or more and contains 12 to 15 pct free moisture. This crude bauxite is crushed to a maximum size of $2\frac{1}{2}$ to 3 in. and is then washed to remove the clay and other impurities present. Generally the washing is performed in scrubbers or trommel-rake washers but locally vibrating screens are used to supplement these.

As the washed bauxite contains about 15 to 18 pct moisture, it is dried before shipment, in rotary kilns that remove all except 1 to 3 pct of the free moisture. The rotary kilns are from 60 to 200 ft long and 6 to 8 ft in diameter, depending upon the size of the operation. They are lined with firebrick. The temperature of the bauxite leaving these kilns is about 200°F. From 20 to 50 tons per kiln hour may be produced. This is the ordinary crushed, washed, and dried bauxite, consisting of mixed lumps and fines, that is marketed for the manufacture of aluminum and for chemical, abrasive and refractory purposes. The main reason for drying the bauxite at the mines is to save transportation costs but drying is important also for the fabricating plants where

the bauxite is to be consumed, as the fine grinding necessary for further treatment during processing requires a dry material.

When bauxite is used for manufacture of abrasives and refractories, it is desirable that the combined water as well as the free moisture should be removed. Therefore some bauxite producers have rotary kilns designed especially for calcining. Such kilns range up to 200 ft or more in length and have heavy refractory linings. The calcining process yields only about 4 to 6 tons of bauxite an hour. The calcined mineral leaves the kiln at a temperature of 1700° to 1800°F .

Tests and Specifications

The bauxite to be used in the various consuming industries differs considerably in composition. To be suitable for the manufacture of metallic aluminum and aluminous abrasives, bauxite preferably should contain less than 2.5 or 3 pct SiO_2 . The iron oxide content is immaterial and may be as high as 20 to 25 pct. When used in the manufacture of aluminous chemicals and refractories, it is important that the bauxite should contain as little iron oxide as possible. Bauxite for manufacture of aluminum sulphate should contain a maximum of 2 pct Fe_2O_3 ; for the manufacture of refractories, it should preferably not contain more than 1.50 pct Fe_2O_3 . For all purposes, it is important that the alumina content be as high as possible consistent with the price.

MARKETING AND USES

As indicated, the main uses of bauxite are in the manufacture of metallic aluminum and aluminous chemicals, aluminous abrasives and aluminous refractories. In a minor way bauxite is used in the manufacture of aluminous cement, in oil filtration and in the smelting of iron. In the manufacture of metallic aluminum, the bauxite is first purified by chemical methods and the resultant product, aluminum hydrate, is calcined to produce alumina. The alumina is smelted to metallic aluminum in electrolytic baths consisting essentially of molten cryolite.

The principal aluminous chemicals produced from bauxite are aluminum sulphate, aluminum hydrate, aluminum chloride and sodium aluminate. Aluminum sulphate is produced by treatment of bauxite or aluminum hydrate with sulphuric acid. Aluminum hydrate and sodium aluminate result from treatment of bauxite with caustic soda. Aluminum chloride is produced by treating heated bauxite with chlorine gas.

Aluminous abrasives are produced by melting bauxite or alumina in small electric furnaces. After solidification and crystallization of this molten product, it is crushed and ground and constitutes the crude abrasive from which grinding wheels, oilstones, abrasive cloths and

papers, abrasive powders and other commercial abrasive products are manufactured.

Aluminous refractories are produced from ground bauxite or alumina by mixing them with a binder, pressing into forms and putting through a baking process. Aluminous refractories, although somewhat more expensive than ordinary fire-clay refractories, are much more resistant to heat, abrasion, corrosion, spalling and erosion, and therefore are being increasingly used where severe furnace conditions are encountered. Fused aluminous refractories of the mullite type are commonly cast directly from the melt.

Aluminous cement is characterized by its rapid-hardening qualities and resistance to chemical action and heat. Aluminous cement is said to reach the same degree of hardness and strength in 24 hr that is reached by ordinary portland cement in 28 days. However, there are certain special portland cements that harden in four or five days, and this has militated against the more extensive use of aluminous cement for general purposes.

Bauxite is said to be effective in desulphurizing, deodorizing and decolorizing oils and other liquids. It is being used commercially for this purpose in the filtering of kerosene. Other uses involving filtration are in prospect. Bauxite is used also as a slag corrective in the smelting of iron.

PRICE

Fig 2 shows graphically the average price at mines of domestic bauxite in the United States as well as the valuation at shipping ports of foreign bauxite used in the United States in recent years, as reported by United States Tariff Commission, War Changes in Industry Series, *Rept. 14* (1946).⁵⁸

BAUXITE RESERVES

More than is perhaps true of most other ores, the estimation of aluminum-ore reserves reflects individual opinion. A variety of raw materials contains appreciable amounts of alumina ranging from 20 pct or less to about 35 pct in clay, shale, anorthosite, nepheline, and leucite rocks; from 30 to 50 pct in aluminous laterite and low-grade bauxite, from 50 to 62 pct in medium and high-grade bauxite, and from 55 to about 75 pct in diasporite rocks. In the presently used commercial aluminum ores ranging in composition from about 50 pct to over 60 pct, the alumina is in the form of the hydrates, gibbsite and boehmite, and is readily extractable. In raw materials with low alumina content, such as clays, shales and various igneous rocks, the alumina is present in the form of silicates and, although extractable, can be recovered only at costs that under present conditions are excessive.

There are enormous quantities of laterite in tropical and subtropical

countries in which the alumina is in the hydrated form, and extractable, but it is generally present in such low percentages that the quantities of material that must be handled in separating the alumina from the associated impurities render the cost prohibitive. The diasporic-bearing rocks, generally consisting of a mixture in varying proportions of diasporic and aluminum silicate minerals, contain alumina in a form not readily amenable to treatment and, therefore, are usable only to a limited extent.

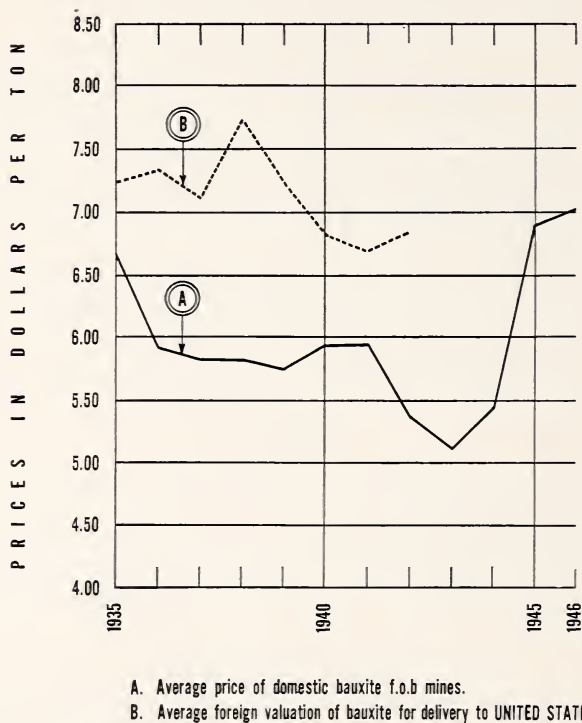


FIG 2--AVERAGE PRICE AT MINES OF DOMESTIC BAUXITE AND VALUATION AT SHIPPING POINT OF FOREIGN BAUXITE USED IN THE UNITED STATES.
From a Report of the U. S. Tariff Commission.⁵⁸

The estimation of aluminum-ore reserves involves the adoption of certain criteria for separating low-grade aluminous materials from materials that may become usable in the foreseeable future. Such criteria may include alumina content and amount and character of impurities, chemical and physical form in which the alumina occurs, and relative extractability, geological relations of the deposits affecting mining, situation of the ore with respect to world markets, and other factors. To calculate reserves of aluminum-bearing raw materials on such a basis evidently requires an intimate knowledge of the major aluminum-bearing deposits. Unfortunately, knowledge concerning sources of alumi-

num-bearing materials is very incomplete and, although fairly detailed studies have been made in some countries during the past five or ten years as a result of the greatly disturbed world economy, the published data are far from discriminative or convincing.

One of the most recent and authoritative estimates holds that the world's aluminum-ore reserves amount to approximately one billion tons.⁵⁸ This is an overstatement if one considers only aluminum ores of present value in respect to the criteria above mentioned. The world's principal aluminum-ore reserves included in the estimate are reported, in percentages, as situated in the following countries: Hungary, 14 pct; China, 14; French West Africa, 10; British West Africa, 8; Jamaica, 7; British Guiana, 6; Nyasaland, 6; Surinam, 5; France, 5; and Brazil, 4. In the aggregate, these 10 countries are believed to contain more than 75 pct of the world's bauxite, the remainder being distributed through 16 other countries.

It is surprising to see prominently mentioned in the list countries in which bauxite mining, if existent, is relatively unimportant.* This is due mainly to the inclusion of low-grade materials unsuitable for use under present conditions but also in part to deposits not yet exploited because of their recent discovery or their isolated position in respect to world markets. Among them are large tonnages of diaspore rocks in China and alumina-bearing ferruginous laterite in French and British West Africa, as well as substantial quantities of low-grade bauxite in the United States, Hungary, Soviet Union, Mediterranean Region, Nyasaland, Australia, and Brazil, and some presently unminable, deep-lying bauxite in France. The extent to which one is justified in disregarding these low-grade materials, which would amount to several hundred million tons, is problematical. It is influenced by possible new discoveries and extensions of known deposits of commercial-grade bauxite as well as by the future trend of the aluminum industry and the development of processes involving the utilization of low-grade aluminum ores. There are large areas in the tropics in both world hemispheres that warrant serious search for bauxite and there is some justification in the belief that future additions to the world's bauxite reserves may exceed unusable low-grade material included in present estimates of bauxite reserves.

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* For comparison, see Fig 2.

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CHAPTER 5

BENTONITE

BY PAUL BECHTNER*

THE name bentonite formerly was applied solely to a peculiar clay occurring in Wyoming and South Dakota, which was distinguished from other clays by its unctuous feel when wet and the property of swelling in water. In the last decade scientific studies of clay have recognized that bentonite is composed mainly of the clay mineral montmorillonite and the name bentonite has been extended to cover the entire family of clays that have montmorillonite as their chief constituent.

Montmorillonite has the chemical formula of $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot x\text{H}_2\text{O}$, with Fe_2O_3 and MgO replacing part of the Al_2O_3 . The montmorillonite crystal is an Si-Al-Si clay mineral, being formed of two silicon-oxygen sheets with an aluminum-oxygen sheet sandwiched between them. In contrast, kaolinite—the chief clay mineral of most clays other than bentonite—is Si-Al, one silica and one alumina sheet. The unit crystal of montmorillonite is much thinner than that of kaolinite, with greater surface area. These differences in crystal structure patterns are leading factors in the dissimilar properties and commercial uses of bentonite compared with other clays.

Minerally, bentonites are 85 to 90 pct montmorillonite with fragments of feldspar, gypsum, calcium carbonate, quartz and traces of other minerals. They vary in color; the widely used Wyoming type is creamy white when dry and a light shade of tan when wet; the low-swelling bentonites of the southern United States and elsewhere are found in many shades of gray, blue, yellow, red, and brown. Pure white bentonites are rarer and generally of the medium or low-swelling type, though there are a few exceptions to that general rule.

PROPERTIES

Bentonites may be divided into two general classes: (1) those that adsorb large quantities of water, "swelling" greatly in the process, and that remain in suspension in thin water dispersions; (2) those that adsorb only slightly more water than ordinary plastic clays or fuller's earths, do not swell noticeably, and settle rapidly in thin water dispersions. Another distinction is that some varieties of the No. 2 type

* General Manager, American Colloid Co., Chicago, Illinois.

can be "activated" by acid treatment to make them highly suitable in oil-refining processes, while type 1 is not activable. Chemical analyses of representative examples of the two main types disclose that the relative proportions of lime and soda are a leading factor in determining physical properties. A high ratio of soda to lime indicates a swelling bentonite while the inverse ratio is usually the nonswelling type.

Intermediate types occur in considerable variety. Some exhibit partial swelling and a few approach the Wyoming type in expansion characteristics but usually are less permanently suspendible in water. "Magnesia bentonite" is an exception to the last statement.

The diverse characteristics of bentonite from different deposits makes it impossible to assign physical properties that will apply to all and when detailed descriptions are given they will be confined to examples of the two types most widely known and used.

The Wyoming (high colloidal, sodium or swelling) type of bentonite has the widest range of commercial uses. The Southern (calcium or nonswelling) type is less versatile but more widespread in occurrence.

Wyoming bentonite, when thoroughly dispersed in water, separates into flakes of which 70 to 90 pct will be finer than 0.5 micron and 5 to 10 pct will be nonsoftening minerals that settle out from dilute suspensions, called "grit." Dispersed Southern bentonite generally yields no more, and often less, than 35 pct finer than 0.5 pct micron and about 30 pct nonsoftening grit. The dispersed unit flakes of Wyoming bentonite have enormous surface area relative to mass, being from 100 to 300 times as wide on their plane surface as they are thick.

This almost unmeasurable thinness offers opportunity for the attachment of other substances available in their environment. The suspendibility and flowability of the flakes in dilute water dispersions give them multiple opportunities for collision with other substances dispersed in the water. The flakes carry net negative charges and bentonites usually display base exchange activity, with Wyoming leading in exchange capacity, acting with organic as well as inorganic cations. The intense response of hydrated Wyoming bentonite to electrolytes is the leading factor in its use for clarification of liquids by coagulation and is also utilized in controlling well-drilling muds.

The sodium bentonite crystal expands ("swells") when water molecules enter between the layers, forming envelopes that are strongly bound to the crystal. When dry, the C-axis dimension of a unit flake is 9.6Å; when saturated it is 21.4Å. In a body of water, the amount seized and held by the bentonite flakes reduces the volume of "free" water, thus causing the internal friction that is measured as viscosity.

Water suspensions of colloidal Wyoming bentonite have a pH of 8.5 to 9.8; nonswelling bentonites have been reported from 4 to 7. Dilute dispersions show Brownian movement and gels have pronounced

thixotropic properties—becoming stiff on standing and reverting to fluidity when shaken.

When subjected to heat, Wyoming bentonite is not affected below 400°F. Above this temperature, swelling and bonding properties are gradually decreased and completely gone at 1200°F. Mississippi bentonite is affected at somewhat lower temperature; reports are lacking on other nonswelling varieties. In “green” bond strength, Wyoming bentonite ranks high among clays, Mississippi very high. In baked and fired strength, the inverse ratio occurs.

DEPOSITS AND PRODUCTION

United States

Bentonite occurs in nearly every state of the U. S. west of the Mississippi River, also in a belt from Kentucky to the Gulf, but commercial production is limited to a few areas. In 1947, the Wyoming-South Dakota area produced 58 pct of the total output of the United States, followed by Mississippi as the next largest. Other states producing bentonite in 1947 were Montana, Texas, California, Utah, and Arizona. The growth of the bentonite industry in the United States is shown in Table 1.

TABLE 1—*Growth of Bentonite Industry in United States*

Year	Total Shipments, Tons	Industrial Usage, Tons			
		Foundries and Steel Works	Drilling Mud	Oil Refining	Other, Uses
1920	2,790				2,790 ^a
1925	14,850				14,850 ^a
1930	82,593	15,580			77,013 ^a
1935	157,445	26,354	32,113	87,822	11,156
1940	251,032	74,135	45,296	95,300	36,301
1946	601,248	162,337	228,474	144,300	66,137
1947	763,889	205,920	237,913	247,609	72,447

^a Distribution of end uses unknown, except for foundry use in 1930.

Foreign Countries

NORTH AFRICA

Development of bentonite deposits began in French Morocco and Algeria in 1942 and after an interruption until 1945 have recently grown to an estimated rate of 20,000 tons production per annum, aided by the monetary exchange situation. Shipments are said to be mainly to France and Great Britain. The cost delivered in Great Britain, calculated in English pounds, is higher than for U. S. bentonite and the

quality is less desirable, nevertheless it has displaced some tonnage from the United States because the exchange situation is more favorable to payment in francs than in dollars.

One of the deposits being worked contains sodium bentonite with blue and yellow strata. The other active deposits contain calcium bentonites of varying color, including one that is white with occasional slight pink or green coloration, like some Nevada bentonites. Some of the calcium bentonites are said to be suitable for activation and there are plans for processing along those lines.

In the field operations, the removal of overburden and digging of the clay are performed by crude, hand-labor methods. The material is stock-piled and taken to Mediterranean ports for shipment. In late 1947 there had been completed a plant to turn out 4 tons per hour of dried and ground sodium bentonite, equipped with a rotary drier and a roller grinding mill following the practice in American bentonite plants.

It was reported that bentonite deposits had been found in Spanish Morocco in 1943 but it is not known whether they are being developed.

GERMANY

Deposits of nonswelling calcium bentonite, similar in appearance and properties to the Mississippi bentonite, occur in the Munich area in Germany, and substantial amounts have been produced. It is said that prior to 1940 more than 70,000 tons per year was shipped in some years. Easily workable surface deposits were mainly exhausted by 1935 and underground mining has since been practiced.

In 1940 there were four processing plants in Germany with a monthly output of 4500 tons of absorbent activated clay, "Tonsil" being the best known brand and one that was widely exported, including small amounts to the United States. The plants also produced up to 2000 tons per month of "Tixoton," an artificial swelling type made by dry-mixing the bentonite with soda ash. It had many domestic uses as a substitute for Wyoming bentonite, to which it was admittedly inferior and higher in cost.

In March 1946, about 600 tons monthly of Tonsil was being produced at one plant and 300 tons monthly of Tixoton at another, the principal outlet being the British Zone of Occupation.

CANADA

There are numerous occurrences of bentonite in western Canada. About 90 pct of the Canadian output comes from southern Manitoba, being a nonswelling calcium bentonite that is said to be of value for oil-bleaching purposes in the natural state and amenable to activation, also suitable for certain classes of foundry use. An activating plant has been in operation at Winnipeg for some years.

The other Canadian output is of a moderately swelling sodium bentonite produced in Alberta and shipped for use in oil-well drilling mud. The total Canadian production in recent years has ranged from 4000 to 5000 tons per annum.

ITALY

A deposit of calcium bentonite, apparently of considerable thickness, occurs on the Isle of Ponza, off the west coast of Italy. Operations started in the early '30s but were not extensive. A few trial lots were shipped to the United States. The bentonite is white in color and resembles the North African white grade in properties. Occurrence of bentonite has also been reported on the Island of Sardinia and in the Provinces of Foggia and Puglie. It is believed that some of the mainland deposits are being developed.

OTHER COUNTRIES

Known deposits of calcium bentonite occur in North Island, New Zealand, and in three places in Australia: Queensland, Western Australia and New South Wales. Some of these deposits are worked in a small way.

Calcium bentonite has been known and probably employed in Japan for many years and is reported to occur also in China and India.

A bentonite called "Askangel" is said to be produced in Georgia, Soviet Union. In Turkey, there has been mention of the "Djebel" deposit. Others have been reported in Poland, Rumania and Czechoslovakia. French statistics indicate production of bentonite but the figures are combined with "bleaching earths," which could be fuller's earth.

Mexico has deposits of fairly white calcium bentonite and Peru, S. A., has a calcium bentonite of varying colors.

MINING AND PROCESSING

Bentonite deposits generally are found in rolling or hilly topography and are disclosed by outcrops uncovered by erosion. Sampling and measuring the extent of the beds is carried on with hand augers or power-actuated auger drills. The usual workable seams are from 1 to 3 ft thick and in the Wyoming-South Dakota area the average of good beds is 30 in. Strip mining is the usual practice and while 10 years ago 2-ft beds with 8 ft of overburden were considered to be the limit of economical digging, such deposits accessible to the processing factories have been mainly depleted; 15 ft of average overburden is now normal and up to 25 ft is removed in spots. Stripping is done with power shovels or draglines but more often with large tractors and bulldozers.

In the beds the highly colloidal (Wyoming type) bentonites contain 30 to 45 pct water; Mississippi bentonites about the same. The deposits in southwestern United States, and many in foreign countries, contain

less water. Digging in the United States is done with power shovels or draglines and the raw clay is transported by trucks to stock piles near the processing plants, which often are from 10 to 25 miles from the diggings.

Except on the surface in hot weather, the raw bentonite does not dry out in stock piles. It is passed through rotary kilns, which are heated by oil or natural gas, and equipped with exhaust fans drawing a large volume of air, and then to storage bins or to grinders or granulators. Air-swept high-speed bowl-type roller mills are the standard machines for grinding bentonite powders with cyclone collectors as necessary adjuncts.

The bentonite most widely used commercially is in the form of 200-mesh powder, weighing about 55 to 60 lb per cu ft and usually packed in multiwall paper bags of 100 lb. Bulkier "micron-sized" powders are packed in 50-lb bags. Dried but unground bentonite, with particles mainly $\frac{1}{4}$ -in. to 20-mesh, is often shipped in bulk carlots. Fine granules of graded sizes are also produced.

TESTS AND SPECIFICATIONS

Because of the variety of types of bentonites and their diverse uses, standard specifications are lacking. The two main industrial uses have tests that do not apply to others. Foundry bentonite is tested according to methods of the American Foundrymen's Association⁴; drilling-mud bentonite by "yield in barrels," gel strength, wall-building and filter rate, which are detailed in various publications.^{3,13}

For other usage, some, not necessarily all, of the following determinations may be useful in evaluations for specific purposes: dry and wet sieve analysis; grit content; viscosity of sols and gels; base exchange, and "swelling."^{2,9}

INDUSTRIAL USES

The Wyoming-type bentonite finds its chief employment in two fields, foundries and oil-well drilling. In foundries it serves as a bond and conditioner for molding sand and its use is standard practice in most U. S. and Canadian foundries as well as in many other countries. In drilling mud it is an almost indispensable ingredient because of its abilities in thickening, suspending, thin-wall building combined with low filter rate, thixotropy. The rapid growth of consumption in the oil fields in recent years is due to the greater depth of wells now necessarily drilled.

Only about 15 pct of the output of Wyoming-type bentonite is used for other than the two main purposes, and their diverse character is interesting. Bonding and plasticizing ceramic and refractory bodies, thermal and acoustical insulation, ore briquettes for smelting operations

and the like, utilize somewhat the same properties as in foundry-sand bonding. Colloidal fineness, suspendibility, dispersability and adsorption qualities fit it into detergents of many kinds and in laundering, especially of heavily soiled articles; likewise in horticultural sprays and insecticides and in the paper and rubber industries. Adsorption of water and swelling lead to uses for impeding leakage in earthworks, masonry structures, mine workings.

Minor tonnages are consumed as a coagulant for clarification of liquids, ranging from wines and sugar liquors to turbid waters and industrial wastes; in wet-mash poultry and stock foods as a thickener; in dermatological compounds as an adsorbent carrier and gel-forming medium; in polishes, water paints, adhesives, asphalt emulsions.

Calcium bentonite is less versatile but has well established commercial applications, the chief one being in oil refining as a catalyst and decolorizing agent, for which purposes it is generally activated by acid treatment, a subject dealt with in the chapter on Bleaching Clay. Mississippi bentonite is developing a rapidly growing outlet in the foundry industry, where it supplements the Wyoming bentonite and has superior properties for some classes of sand molds.

An important tonnage of Wyoming-type bentonite is exported, being used in nearly all industrialized countries, especially by foundries. Substantial shipments of it for drilling mud are made to countries where oil-well drilling is in progress. Activated Southern bentonite also has a considerable foreign market.

The bentonites produced in other parts of the world follow the known uses for calcium, nonswelling type. The only known foreign deposit of sodium bentonite is one recently opened in Algeria and this is too new to be evaluated as a permanent source.

PRICE HISTORY

Bentonite is prepared and marketed in many forms and grades, which sell at different prices, but the history of the kind best known to the consuming trade, 200-mesh powder, will serve as an illustration. In 1930 it sold at \$18 per ton and declined to \$11 in 1935 because of larger production and sales. In 1941, it was \$8.50 to \$9.50, then gradually rose to \$11.50 per ton in the latter part of 1948. These figures refer to carlot shipments in domestic paper bags f.o.b. producing points and represent good marketable quality but not special gradings, which sell up to \$18 per ton. Packed for export, the price of standard 200-mesh material is \$14 to \$18 per ton, depending on style of packing. The dried, unground product in 1948 was priced at \$8.50 to \$9 in carlots in bulk, not bagged.

Mississippi bentonite, 200-mesh unactivated, sold in 1948 at \$13.50 per ton in carlots f.o.b. shipping points. Prices of foreign bentonites

are not available but are said to be higher than the corresponding clays in the United States.

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CHAPTER 6

BLEACHING CLAY*

By A. D. RICH†

THE term "bleaching clay" or "bleaching earth," as used in the oil industries, refers to clays that in their natural state, or after chemical or physical activation, have the capacity for adsorbing coloring matter from oil. There are three common types of bleaching clays: fuller's earth, activated clays, and activated bauxite.

Fuller's earth, or naturally active clay, is prepared from bentonites that possess natural activity. It is not activated commercially; in fact, earths of this type ordinarily do not respond satisfactorily to acid activation. Fuller's earth is prepared in pulverized as well as granular form for use in the contacting and percolation processes, respectively.

Acid-activated clays also are of bentonitic origin. The basic raw clay, however, is of a type that has a very low natural activity but is highly activable by treatment with mineral acid. Commercial acid-activated clays generally possess several times the decolorizing power (bleaching efficiency) of the best quality of fuller's earth. The former are prepared commercially only in the pulverized grade because of the difficulties in obtaining a satisfactory granular product, and hence are used only in the contact process.

Activated bauxite is made by heat-treating bauxite ore, which in its natural state has very little natural activity. The commercial product is prepared in granular form for use in the percolation process on petroleum oils.

For the most part, bleaching clay is used commercially in the decolorization of animal, vegetable and petroleum oils, fats and waxes. It is applied in two ways: (1) by the percolation method and (2) by the contacting method. Percolation refers to the passage of oil through a bed of granular clay whereas contacting refers to direct agitation of oil and pulverized clay followed by removal of the clay from the oil by filtration. In either case, the decolorizing effect is obtained by inti-

* This chapter is a revision and an expansion of the review of the same subject by J. W. Bell and S. R. Funsten, which appeared in the 1937 edition of this volume. Data taken from article on Mineral Absorbents, by R. B. Secor and G. A. Mickelson, of the Filtrol Corporation, to appear in Vol. 3 of the Encyclopedia of Chemical Technology, are gratefully acknowledged.

† Filtrol Corporation, Los Angeles, California.

mate contact between the liquid oil and the solid adsorbent. Petroleum oils are treated commercially by either the percolation or the contact process. Animal and vegetable oils are treated by the contact process only.

COMPOSITION

The raw clays from which both fuller's earth and acid-activated clays are prepared are composed of hydrous aluminum silicates containing varying quantities of magnesium, iron, calcium and other elements. These raw materials are usually nonswelling bentonites derived from volcanic ash or lava by weathering and hydrothermal chemical reactions. The bentonites have as their chief mineral constituent montmorillonite, which has the ideal formula $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2n\text{H}_2\text{O}$. The underlying reasons are not fully known for the natural activity of the fuller's earth type of clay and its usual failure to further activate with mineral acid in contrast to the natural inactivity of the activable type of clay. However, it may be said that the bentonites that are responsive to the acid-activation treatment generally have not undergone any drastic metamorphism.

The chemical composition is not a reliable means of discrimination between a nonactive, a naturally active, and a nonactive but activable clay, therefore it is not possible to forecast the ultimate quality of a clay on the basis of the raw-clay analysis alone. Table 1 gives typical analyses of representative clays of the foregoing classifications.

The term "bauxite" is used to designate an ore or a soft unconsolidated rock deposit with a high percentage of aluminum, which is present as gibbsite, the trihydrate, or as boehmite, the monohydrate. The composition varies appreciably within a single deposit or between deposits. As with bentonites, the composition of the raw material cannot be utilized to determine ultimate adsorbent efficiency.

PROPERTIES

Properties of bleaching earths from different parts of the country, or even in different parts of one deposit, frequently vary over a considerable range, therefore it is necessary to generalize in discussing this subject.

The fuller's earth type of clay is characterized by a lack of plasticity, high water content, foliated structure, and tendency, when water is removed from the clay, to adhere strongly to the tongue. Most of the best fuller's earths show a high silica to aluminum ratio, varying from 4 to 6. Another property is a relatively high hydrous silica content, which may have a bearing on the decolorizing efficiency. Some commercial fuller's earths, such as Pike's Peak clay from Georgia, Japanese acid clay, and English fuller's earth, possess an apparent acidity. While they contain no free acid, they have the ability to adsorb alkali in a

water slurry before giving a pink reaction with phenolphthalein. The effective cations appear to have been replaced by hydrogen in the natural state. Color and texture of fuller's earth are so variable that no generalizations can be made.

TABLE 1—*Typical Analyses of Clays*
COMPUTED ON PERCENTAGE BY WEIGHT

Constituent	Nonactive Clays			Naturally Active Clays		Activable Clays	
	Siliceous Fire Clay	Florida Kaolin	High-diatom Clay	Fuller's Earth		Acid-activated	
				Georgia	Florida	Raw	Activated
SiO ₂	72.05	45.67	71.35	53.42	52.92	50.20	58.30
TiO ₂		0.10	0.47	0.52	1.18	0.20	0.34
Al ₂ O ₃	17.21	38.45	11.45	10.06	9.42	16.19	15.34
Fe ₂ O ₃	1.25	0.75	6.93	3.58	3.65	4.13	1.01
MgO.....	0.75	0.05	2.00	9.18	9.08	4.12	3.47
CaO.....	0.45		1.79	1.29	1.91	2.18	1.18
Na ₂ O.....			0.13	0.02	0.03	0.17	None
K ₂ O.....		0.06	0.24	0.64	0.98	0.16	None
P ₂ O ₅			0.57	0.12	1.21		0.08
CO ₂			tr	0.05	0.11		tr
Cl.....			None	0.03	0.03		
SO ₃			None	0.02	0.04		
Ignition loss ^a	8.56			9.42	10.19	7.57	4.81
Uncombined water...		14.86	5.30	11.83	9.06	15.58	15.77
Total.....	100.27	99.94	100.23	100.18	99.79	100.50	100.64

^a Not including the uncombined water.

The apparent density of fuller's earths is somewhat lower usually than that of the acid-activated or ordinary kaolinite clays. Fuller's earth from Georgia and Florida usually weighs 30 to 40 lb per cu ft when processed, compared with 40 to 50 lb per cu ft for the acid-activated clays. Minerals found present in some fuller's earths include attapulgite, illite, nontronite, and kaolinite, in addition to montmorillonite.

Acid-activable clays differ from fuller's earth in that the former generally have a waxy appearance and that they slake or rapidly disintegrate in water; also, activable clays do not stick to the tongue as readily as do fuller's earths. They do not swell appreciably in water. The base exchange positions usually are occupied by calcium and magnesium ions. Clay minerals present may include beidellite, saponite (hectorite), and nontronite in addition to montmorillonite, the chief mineral constituent. Small amounts of kaolinite, hydrous silicic acid,

unweathered volcanic ash, calcium carbonate, and sand are often present as impurities. The nature and quantity of these impurities have an important bearing upon the performance of the finished adsorbent.

Theories of Behavior of Bleaching Clays

The theory of the action of bleaching clays in decolorizing oils is highly involved and the underlying reasons for the phenomenon are not completely known. Suffice it to state here that the action is not a straining or filtering action but a selective adsorption of the color bodies and other impurities. The adsorbed color bodies and impurities are strongly held within the clay structure and can be removed only by drastic treatment. This indicates that the bleaching clays operate mainly by chemical adsorption. The literature should be consulted for a thorough investigation of the subject.

DISTRIBUTION OF DEPOSITS

Deposits of bleaching clay are well distributed throughout the world but more clays and larger deposits have been found in the United States than elsewhere. Principal deposits of fuller's earth in the United States are found in Florida, Georgia, Illinois, Texas, California, and Nevada. Important sources abroad are England and Japan. Clays susceptible to activation to a high degree have been found domestically in Arizona, Mississippi, California, New Mexico, North Dakota, Nevada, and Texas. Abroad such clay deposits are in Germany, Rumania, Morocco, Russia, Canada, Italy, England, Argentina, Japan, Hungary, and elsewhere.

Bauxite deposits in the United States are rather limited. Commercial deposits are found in Arkansas, Georgia, and Alabama. The more important deposits abroad occur in France, England, Dutch Guiana, British Guiana, Gold Coast, India, Rumania, Hungary, Italy, and Yugoslavia.

PRODUCTION AND CONSUMPTION

Bleaching earth has been used in various ways for centuries. The Chinese used it to decolorize oils more than 1000 years ago. Mention of it is made in the Bible and in the writings of Pliny. Fuller's earth was mined in England in the middle of the nineteenth century but it was not until 1880 that the product was imported for commercial use in the United States. The first American fuller's earth deposit of commercial importance was discovered at Alexander, Arkansas, in 1891, and a few years later the extensive Georgia and Florida deposits were found.

Acid activation of clays was started about 1905, in Germany. The German industry rapidly expanded during World War I, when English fuller's earth importations were cut off. Accurate production fig-

ures for the Germany industry are not available but it is estimated that the annual tonnage prior to World War II was in the neighborhood of 35,000 to 40,000.

The acid activation of clay on a commercial scale in the United States started during World War I and in 1922 the product "Filtrol" appeared. Abroad, acid-activation plants are located in England, France, Italy, Rumania, Switzerland, and Japan, besides Germany.

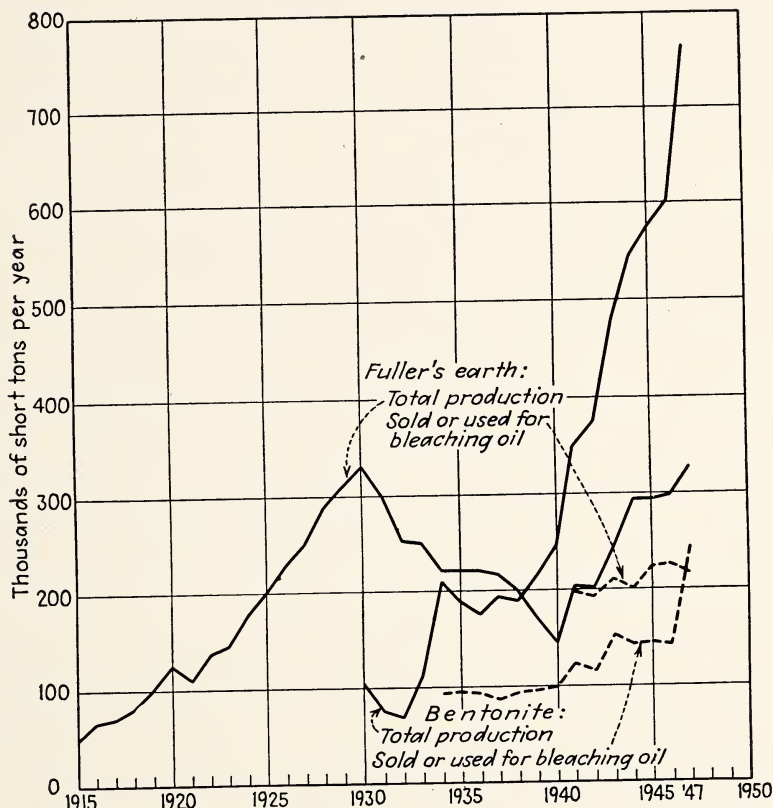


FIG 1—TRENDS IN DOMESTIC PRODUCTION OF FULLER'S EARTH AND OF BENTONITE.
From Minerals Yearbook, U. S. Bureau of Mines.

Activated bauxite has been used for a long time abroad but it did not become available in the United States until 1936. It is widely used in the eastern part of the country and has replaced some of the percolation grades of fuller's earth, over which it possesses some distinct advantages for certain petroleum oils.

Fig 1 shows the trends in production of fuller's earth and bentonites in the United States in recent years. The tonnage of fuller's earth employed in bleaching oils was almost the total tonnage until 1942, when new applications for the product suddenly developed under the stimu-

lation of the war. These included uses as an adsorbent and for rotary drilling. By 1945, adsorbents used 19 pct of the domestic fuller's earth production; rotary drilling, 4 pct; petroleum-oil bleaching, 65 pct; vegetable and animal-oil bleaching, 9 pct.

The bentonite tonnage indicated in Fig 1 for oil refining is largely made up of the crude bentonite, which subsequently is acid-activated to produce activated bleaching clays. In the early 1930s, as much as 50 to 60 pct of the total crude bentonite produced in the United States was employed in bleaching oil. Because of the much greater increase in tonnage for other uses since that time, the proportion of bentonite used for bleaching oils is now only about 25 pct of the total, although it also has increased to some extent.

PROSPECTING, EXPLORATION AND MINING

Prospecting and Exploration—The United States Geological Survey and various state geological surveys have made a rather extensive study of bleaching earths in the United States and various publications give details as to the location and nature of deposits covered in these studies. The relatively low value of bleaching earth makes it of little interest to the individual prospector. Most of the large companies do this work as needed. Many samples are received by these companies from land-owners, and if the tests show promising results the deposits are inspected and samples obtained by opencut methods or by use of hand core drills. Since the quantity of naturally active and activable clays in the United States is far in excess of any conceivable demand, prospecting and exploration are limited to properties for which location and mining conditions are particularly favorable.

Mining Methods—Mining of bleaching earths for the most part is by the opencut method. The overburden, ranging from 5 to 50 ft in depth, is removed either by steam shovel or dragline to within approximately one foot of the top of the clay. The remaining foot of overburden is removed carefully by hand or mechanical means. It is the usual practice to lay out the area carefully before beginning work, so as to evaluate fully the quality and amount of material to be mined. Whenever possible, mining is done in dry weather, in order to avoid excess handling of moisture. When the clay strata are too deep for opencut mining, a tunnel method is used, very similar to that used in coal mining.

Great care is taken in mining to eliminate foreign material such as limestone or other rock. The water content of clay as mined depends largely upon the location and type of clay. The amount of uncombined water in southeastern clays as mined is approximately 50 pct by weight while in the Arizona and California clays it varies from 20 to 30 pct by weight. In some instances the lump clay is handled from the mine

to the mill in mine dump cars, but when the distance is too great the material is transferred generally by truck and rail. When weather conditions permit, much of the water is removed from the clay by air-drying before it is transferred.

PREPARATION FOR MARKET

Fuller's Earth

When the bleaching earth is to be used in the natural state without activation or granulation, preparation for market is comparatively simple. It is necessary only to pass the raw lump clay through a crusher, dry the crushed clay by means of a gas, wood, or oil-fired rotary drier, and finally to grind the dried clay to the desired size. Dust losses are insignificant because little money is spent on the material. It is impor-

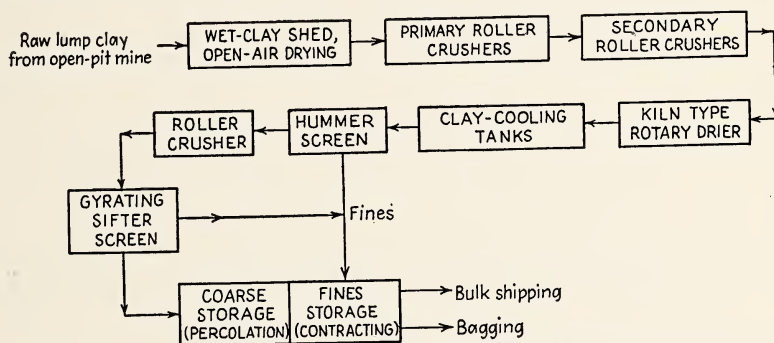


FIG 2—FLOWSHEET OF FULLER'S EARTH MANUFACTURE (PERCOLATION GRADE).

tant to maintain careful technical control of temperature and time in the drying operation, because the clay can be injured greatly by incorrect handling. Experience has shown that a free moisture content of from 8 to 10 pct gives the greatest efficiency for natural clays of the contact type. This corresponds approximately to a total volatile content of 15 pct. The preparation of granular fuller's earth is somewhat more complicated.

The procedure in a typical fuller's earth plant in the United States is as follows: After the raw clay has been air-dried for two or three days, it is loaded into two portable distributors, each equipped with a hopper bottom and a steel-plate apron conveyer. The clay is fed at a uniform rate by the distributors onto a 24-in. inclined belt conveyer that discharges into two or more roll crushers, which reduce the clay to a maximum size of 2 in. From the primary roll crusher, it passes to bucket elevators that discharge it to five secondary crushers, which reduce it to a maximum size of 1 in. Oil-fired rotary driers housed in an adjoining building follow each set of crushers. The clay, in passing through a drier, is lifted by longitudinal interior channel irons and

dropped through hot gases. In the 20 minutes required for the clay to pass through a drier, its volatile content, including moisture, is reduced from 40 or 50 pct to a maximum of 15 pct. Chain drag conveyers of the bucket type move the product of the driers to three clay-cooling tanks, which are well ventilated to carry off suspended dust, heat and moisture. By means of chain bucket elevators, the clay discharges into the tops of the two tanks of larger diameter. Through a series of feed-regulating gate valves in the bottoms of these tanks, it passes onto a conveyor belt, discharging into the top of the third tank, which has a hopper bottom and a mechanical feeder through which a uniform quantity of clay is fed to an electrically vibrated Hummer screen of $\frac{1}{2}$ -in. mesh. The oversize, after being reduced in a high-speed roller mill, joins the undersize and passes directly to a belt conveyor equipped with a magnetic head pulley, which removes all tramp iron. The clay is then taken to the top of the mill building by a bucket elevator of the belt type, and passes in two equal streams on each side of a fire wall that is built on the center line of the building. Operations on each side of the wall are identical but distinctly separate from each other. The initial separation in the mill building is made by a Hummer screen of the same type employed under the clay-cooling tank. Reduction is effected in roller mills, which consist of duplicate sets of corrugated rolls. From each set of rolls, the material is conducted to a silk-dressed gyrating sifter. Handmade silk of Swiss manufacture is used in these sifters. It is exceptionally uniform in quality, is durable and can be repaired readily. The oversize, or tailing, from each sifter passes directly to another set of rolls for further reduction and screening. This operation continues until the material has been reduced to the required mesh. After screening, the clay passes to a series of hopper-bottom bins, in which the various sizes are stored. Shipments are made in bags and in bulk.

For bag shipment, the clay is weighed automatically and filled into bags of the best quality of burlap, usually 135 lb to a bag. The bags are sewed shut, tagged, transported by hand truck to the shipping platform and placed in cars with the long dimension horizontal. Carloads consist of 25 to 35 tons. Bags are the property of the producer and are credited on the consumer's account when they are returned in good condition. Milling practice in general is similar to that employed in milling wheat. The object of gradual reduction is to limit as much as possible the percentage of fines, the principal market demand being for the coarser or granular grades. Grain-type freight cars are used for both bag and bulk shipments.

Activated Clay

The manufacture of an activated clay is more complicated than the manufacture of the granular fuller's earth (Fig 3). There are seven

important steps in the process: (1) preparing the raw clay for charging to treaters or reaction vessels; (2) activating; (3) washing out impurities; (4) dewatering mechanically; (5) drying; (6) grinding to proper mesh size; (7) packaging.

The raw clay for charging to treaters may be prepared by either wet or dry method. When the wet method is employed water is added to the raw clay, which is already high in moisture, until it forms a slurry or thick slime, which is then conveyed to treaters by pumps or gravity. When the so-called dry method is employed, much of the free moisture is removed from the clay by a predrier. The dried clay is then usually conveyed by belts to a mixer, where water is added in order to make a slurry as it enters the treaters. Different methods are employed, depending upon the nature of the clay. Sometimes, instead of using ordinary water for making a slurry, a "sour" water or return liquor from the washing system is used. The clay and water, or liquor, are accurately measured before going to the treaters. The acids used for

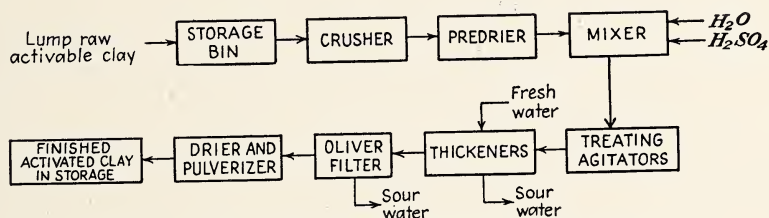


FIG 3—FLOWSHEET OF PROCESS FOR ACTIVATING CLAY.

the activation are usually sulphuric or hydrochloric, generally sulphuric in this country, because of its lower cost. The acid usually is added to the slurry as it enters the treaters, although sometimes it is added during mixing or after the charge has entered the treaters. The proportion of acid varies according to its concentration and the nature of the clay. Steam is used to bring the charge to boiling point and during the treatment the temperature is kept between 212° and 220°F. The charge is kept in constant motion during treatment by means of air or mechanical agitation. The length of time of treatment varies with the nature of the clay and the quantity and concentration of the acid; usually it is between 2 and 12 hr.

The so-called continuous method of treatment is sometimes employed. In this a proper mixture of the clay, water and acid moves in the form of a slurry from one treater to another in a series, as many treaters being used as are required to give the proper time for activation. All treaters must be made of or lined with corrosion-resisting materials.

After the activation has been completed, the slurry is conveyed

to a countercurrent thickened system, where the water-soluble constituents are removed from the clay. A thickener system consists of a number of tanks connected in series, one elevated slightly above the other. In each tank there is a shaft to which are attached at the bottom a number of rakes, usually four. The shaft is suspended in the center of the thickener and the rakes reach nearly to the outer edge. The speed of revolution of the shaft varies according to the settling rate of the solids. On the bottom side of the rakes are numerous blades set diagonally. As the solids settle they are dragged by the blades slowly to the center of the thickener, where they drop into a cone, from which they are conveyed through a pipe line by means of a diaphragm pump and discharged into the thickener next higher in the series. This operation is repeated through all thickeners of the system. At the same time there is uniform flow of fresh, soft, hot water entering the highest thickener of the system and moving down through the entire series, carrying with it a large part of the free acid, dissolved salts, and other impurities that have been separated from the solids. Sometimes the washing is done by means of filters and fresh water in a batch system and sometimes by filters connected in series in a continuous system. All pumps and lines used for conveying concentrated slurries must be of corrosion-resisting materials. For this purpose Duriron and lead have been very satisfactory.

From the thickener system, the slurry is transferred either by pump or gravity to a continuous vacuum filter. The effluent is pumped away for further use in washing the slurry, or is discarded. The cake from the filter is conveyed to a drier, where its uncombined moisture is reduced to approximately 15 pct. The dried material goes to a grinder and is pulverized to the size desired. Sometimes the drying and grinding are done in the same equipment. After the material has been ground, it is usually packed by bagging machines into multiwall paper bags. Some are of the self-closing valve type and others are of the open-mouth type. When the latter are used the charge is weighed in the bagging machine and dropped into the bag and the closing is done by a sewing machine, which is part of the equipment. Multiwall paper bags have been used for activated clay during the entire life of the industry in the United States. They are used for shipments to all continents and are accepted by all classes of carriers.

Technical control of plant operations is essential at each stage in the process, in order to ensure a uniformly high quality of the final product.

Bauxite

The selected crushed ore is dried first at 200° to 300°F, then the dried bauxite is separated by screens and is ground in such a manner as to obtain the maximum yield of coarse matter from percolation

grades. It is next calcined at the optimum temperature for the particular application, ranging anywhere from 600° to 1600°F. Conditions of calcining are very important. Temperatures of 1200° to 1600°F are often required to obtain maximum efficiency for percolation of petroleum oil.

In the latter process, the activated bauxite may be revived by treating with solvents, steaming, and calcination. This removes carbonaceous matter and reactivates the surface and it can be repeated a number of times without appreciable loss in decolorizing power of the adsorbent.

TESTS AND SPECIFICATIONS

The specifications for bleaching earths depend largely on the nature of the work to be done. For refining vegetable, animal and mineral oils by the contacting method, a finely pulverized clay is used, having a mesh of at least 50 pct through 200 and generally from 85 to 95 pct through 200. The limiting factors on fineness are filter rate, or the speed with which the oil can be separated from the clay cake after contacting, and oil retention. If too much impalpable powder is present, the filter rate may be retarded to a point unsuitable for use in refining and the oil retention may be so high that losses of oil in the press cake may become excessive. Therefore, while it is an advantage from the standpoint of rapidity of decolorizing action to employ fine-mesh clay, the degrees of fineness must be held within definite limitations. When the percolation method is used, a coarse mesh is required in order to permit free passage of the oil through the clay. The most popular percolation grade is that known as 30/60 mesh. Other standard-mesh percolation grades are 60/90 and 15/30. Aside from meshing, the specifications for naturally active clays are very similar, whether they are contacting or percolation grade.

TABLE 2—*Typical Tests on Representative Clays*

Data	Fuller's Earth, Florida-Georgia Type		Natural Bleaching Clay, Southwest Type, Fine Grade	Acid- activated Clay, Domestic Type, Fine Grade
	Fine Grade (Con- tacting)	Coarse Grade (Perco- lation)		
Volatile matter, pct.....	16.0	16.5	16.0	21.0
Density, lb per cu ft.....	31.0	35.0	53.0	45.0
Acidity, mg KOH per gram.....	Neutral	Neutral	Neutral	3.5
Screen test, pct through 200-mesh.....	95.0		70.0	88.0
Mineral-oil decolorization value (efficiency $a = 100$ pct), pct.....	100		40-110	250-500

Table 2 gives typical physical tests of a naturally active, commercial, southeastern fuller's earth of fine and coarse grades, of western natural clay, and of fine-grade acid-activated clay. This table refers to physical tests only because the most important specification for a bleaching earth is its decolorizing value. Tests commonly applied in the bleaching-earth industry are outlined in the following paragraphs.

A. Physical and Chemical Inspection Tests Applicable to both Natural and Artificial Activated Clays.

VOLATILE CONTENT—The percentage loss in weight of a given sample of clay after ignition at 1800°F for 10 minutes.

MOISTURE CONTENT—The percentage loss in weight of a given clay sample upon drying to constant weight at 220°F.

VOLUME WEIGHT OF CLAY—The volume occupied by a given weight of clay after 5 minutes mechanical tamping time, in a graduated cylinder, the results being expressed in pounds per cubic foot.

SCREEN ANALYSIS—The weight per cent of clay retained by and passing through each of a series of standard measuring screens using the conventional Ro-Tap.

ACIDITY—The weight of potassium hydroxide in milligrams required to neutralize a distilled water extract from one gram of clay, phenolphthalein being used as an indicator.

OIL RETENTION (contact-grade clays only)—The increase in weight of a given quantity of clay after contacting with oil and blowing the cake produced with air under definite prescribed conditions.

B. Activation Methods

Natural bleaching clays, exhibiting potential activable characteristics, are activated by treatment in weak acid (i.e., 8 to 20 pct) at boiling temperature for 6 hr, washing the residual slurry free of acid and soluble salts, drying to 20 pct volatile content and pulverizing the treated dry product.

C. Decolorization Tests

PERCOLATION-GRADE CLAYS—The decolorizing power of percolation-grade clay is determined by permitting a standard oil stock to pass through a column of granular bleaching clay and measuring the volume of filtrate obtained at a given composite filtrate color. By comparison of this yield with the volume of filtrate obtained under identical conditions through the use of a clay of known decolorizing power, it is possible to determine the efficiency of the unknown clay as compared with the standard.

CONTACT-GRADE CLAYS—The decolorizing power of the contact-grade clays is gauged by determining the color produced by mixing the clay with a standard oil stock, agitating the mixture at a given temperature, and filtering the clay from the oil. Knowing the amount of a standard clay required to produce the same color, the decolorizing power of the clay being treated can then be expressed as a percentage of the standard.

Since there is no single oil standard by which efficiency of the various earths can be gauged, the relative values of competitive clays must be established on representative commercial oils. The importance of oil-retention value of the competitive earths is second only to decolorization value, since the oil held up or adsorbed in the clay after

use is not customarily recovered and therefore the loss must be charged off to the operation when the clay is discarded. This particular test is not so important with the percolation-type clay, because revivification is generally practiced, but it is of utmost importance for contacting clays, where oil frequently is not recovered from the spent cake. A great advantage for chemically activated clays is the low oil retention,

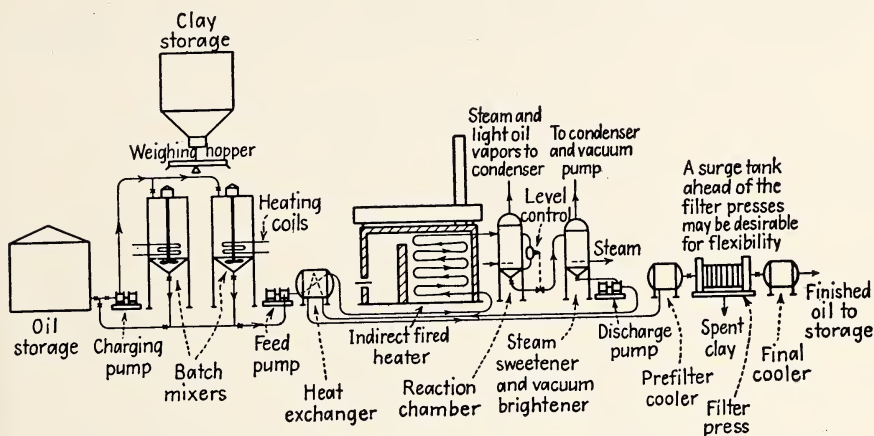


FIG 4—FLOW DIAGRAM FOR CONTACT FILTRATION PLANT.

owing to the fact that only a small quantity of material is required to obtain decolorization.

MARKETING AND USES

Fig 4 shows a typical contact filtration plant for processing mineral oils with bleaching earth. This plant is semicontinuous and differs from the plants for bleaching vegetable and animal oils, which generally are batch operations. Fine-grade clay (100-mesh and up) is used exclusively in contact filtration plants. A typical percolation process for refining mineral oils is shown in Fig 5. Among the principal types of oil refined in the mineral-oil field are naphthas, fuel oils, lubricating oils, waxes and greases. The more important vegetable and animal oils to which bleaching clays are applied are cottonseed, soybean, linseed, coconut, palm, tallow, and grease.

The principal object of applying bleaching earths is to remove color but there are increasingly important uses in all fields of refining that do not involve removal of color; for instance, in treatment of naphtha, reduction of the amount of gum and stability are more important factors. In refining of lubricating oil, improved sludge content, carbon content, oxidation test, acidity, emulsion test, viscosity index, and other factors, are often more important, and in the vegetable-oil field, stabili-

zation and removal of residual soap, gums, odor, and taste are often the more important factors.

Some of the results secured with bleaching earths can be accomplished in part by other means of refining, such as treating with solvents or acids, hydrogenation or fractionation, but the relatively low cost of the bleaching-earth process makes it extremely advantageous.

Deliveries of bleaching earth are made both in box and tank cars but for the most part the clay is shipped in paper or burlap bags. Because of the wide variation in uses and type of equipment employed

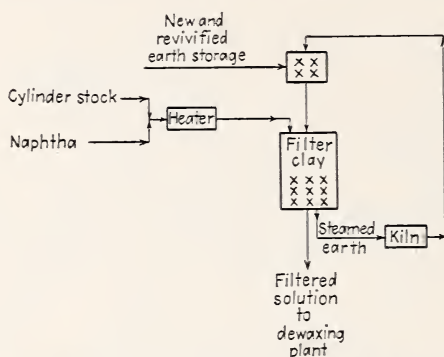


FIG 5—PROCESS FOR MINERAL-OIL PERCOLATION (CYLINDER STOCK SOLUTION).

throughout the country, producers of bleaching earth maintain adequate staffs of experienced engineers to offer technical service to the customer.

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CHAPTER 7

BORAX AND BORATES

BY GEORGE A. CONNELL*

BORAX, a sodium borate and the principal sodium salt of boric acid, has been surrounded with romance and with a certain amount of mystery. Its early history is not entirely known but it has been contended that Marco Polo in his travels in the Orient introduced this material to the West during the Middle Ages. Without doubt its first source was from Central or Eastern Asia and perhaps from Tibet. The well-known fluxing properties of borax probably introduced its earliest use, that of a soldering flux in the manufacture of jewelry. This use, as well as the remote location of most borate deposits, added greatly to the romance associated with the thought of borax.

COMPOSITION

The common element in all borates is boron but this element has never been discovered as such in any deposit, because of its great affinity for oxygen. Incidentally, this makes its manufacture extremely difficult and expensive. Elemental boron undoubtedly has many properties that make it quite valuable but the extreme cost involved in producing it from its oxidized form prevents its general use or manufacture.

Many minerals contain boron; more than 50 have been listed and, excepting nine, they all contain water of crystallization or composition. Borates can be defined as minerals containing an oxide of boron, and usually water of crystallization, and include boric acid as well as metallic salts of boric acid.

Borax is the most important borate mineral both as a raw material and as a refined chemical. Chemically speaking, it is the decahydrate of disodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), and, further, can be considered as the acid salt of monosodium metaborate. However, the term "acid salt" might imply that borax gives an acid reaction in solution, which is not true, since solutions of borax are decidedly alkaline, giving a pH of 9.2.

Boric acid, also known as boracic acid, has the chemical formula H_3BO_3 ; it occurs in nature as the mineral sassolite. Sassolite has been

* Vice President, Pacific Coast Borax Co., Los Angeles, California.

mined and used both as a source of boric acid and as borax, although its occurrence as a natural mineral is relatively rare. Refined boric acid, however, is the second most important borate mineral from an industrial and chemical standpoint.

From borax and boric acid, other commercially important borates are made, such as monosodium metaborate ($\text{NaBO}_2 \cdot 4\text{H}_2\text{O}$), potassium pentaborate ($\text{K}_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$), ammonium baborate ($(\text{NH}_4)_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$), ammonium pentaborate ($(\text{NH}_4)_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) and sodium perborate ($\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$).

The naturally occurring borates may be divided into three groups: (1) those containing no water, (2) those containing water but no silica and (3) those containing water and silica. Of these the most important group commercially is the second, which contains six minerals having particular commercial significance; that is, borax (tincal), kernite (rasorite), colemanite (borocalcite), ulexite (boronatrocalcite), priceite (pandermite) and sassolite (boric acid).

TABLE 1—*Important Borate Minerals*

Mineral	Formula	Boric Oxide, Pct	Boric Acid, Pct
Borax.....	$\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$	36.5	64.8
Kernite.....	$\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$	51.0	90.5
Colemanite.....	$2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$	50.8	90.3
Ulexite.....	$\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 16\text{H}_2\text{O}$	43.0	76.3
Priceite.....	$4\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$	48.9	88.5
Sassolite.....	H_3BO_3	56.3	100.0

PROPERTIES

Borax (tincal) in deposition is found as individual crystals, as aggregates of poorly developed crystals, and as compact glassy masses showing no crystal faces. When pure, borax is clear and colorless, but much of it is dull, earthy white. This earthy color is due to the partial dehydration to the lower hydrate tincalconite and, owing to enclosed mud, may even be gray or dark opaque. The crystals are monoclinic and have several cleavages but the natural mineral seldom shows cleavage faces when broken. Its hardness is 2 to 2.5 and its specific gravity is 1.72. Borax is soluble in water; although its solubility as well as its rate of solution is low at cold temperatures, it increases rapidly in hot water, and borax is completely soluble (melted) in its own water of crystallization at 77°C . When heated above this temperature a crystal of borax will lose its water of crystallization and finally becomes anhydrous at 740°C . On cooling it becomes a glass (borax glass) or, under special conditions, crystalline.

Kernite (rasorite) occurs in clear, colorless monoclinic crystals

as much as several feet in diameter and in cleavable masses of similar size. Two perfect cleavages and several other planes of separation cause the mineral to break rapidly into small pieces and fibrous aggregates. The mineral somewhat resembles selenite gypsum in general appearance. The hardness is 2.5 and specific gravity 1.95. The rate of solution of kernite is very much slower than that of borax. This applies both at low and high temperatures.

Colemanite (borocalcite) occurs in shining crystals, colorless to white, and also as white to gray compact granular masses. Its hardness is 4 to 4.5 and specific gravity is 2.42. The mineral is insoluble in water but soluble in acid. When heated it decrepitates to a powder, a characteristic property.

Ulexite (boronatrocalcite) is not found in distinct crystals but forms either rounded aggregates of radiating acicular fibers (cotton balls) or solid masses of parallel or radiating white fibers with a silky luster. The hardness is 2 and specific gravity is 1.96. Ulexite is not soluble in cold water but is slowly attacked by hot water and is readily soluble in acids.

Priceite (pandermite) occurs in massive formations; it is almost amorphous in form and in appearance is white, quite similar to marble; hardness is 3, specific gravity, 2.4. Priceite is insoluble in water but soluble in acids. Crystals that occur are triclinic.

Sassolite (boric acid) is found in rather flat crystals and when pure is clear and colorless. Its hardness is 2 and specific gravity is 1.49. Sassolite is soluble in water, its solubility increasing with rising temperatures. The crystals are triclinic. When heated above 100°C, it loses part of its water of composition and changes to metaboric acid. Upon further heating it loses all of its water and forms an amorphous product known as anhydrous boric acid or boric oxide. In solution sassolite gives a slightly acid reaction.

DISTRIBUTION OF DEPOSITS

Of the six present commercially important borate minerals, four occur in California and Nevada in relatively large deposits; that is, borax, kernite, colemanite, and ulexite.

Although California probably is the present largest source of borates, large deposits occur in other countries. Ulexite is found in South America in Peru, Chile, Bolivia, and Argentina. Priceite (pandermite) occurs in commercial deposits in Turkey and is being mined today. Sassolite in solution occurs in the *suffoni* of Italy and supplies some of the boric acid needed in Europe and elsewhere. Stassfurtite occurs in Germany; crude tincal is found in Tibet, and ulexite has been found recently in Iran. As far as is known, all of these deposits are being commercially operated today.

The following data on Russian borates was published in *Die Chemische Industrie* (Oct. 25, 1940) Nos. 42/43, 623-624.

"Until 1936, the Soviet-Russian industry of boron compounds was dependent on imports of foreign raw materials, mainly crude sodium borate. Since then, the exploration of the Inder Lake deposit, discovered in 1934, has been started. As a result, the raw material situation has changed entirely and become independent of foreign sources. This deposit is situated east of the Ural River between the Caspian Sea and the city of Uraljak. It carries besides high-grade boron minerals (principally ascharite and hydroboracite), which are worked at present, also poorer ones, the treatment of which is contemplated. Furthermore, some time ago, it was found that the so-called 'deep brine' of the Inder Lake, with which the 36-meter thick salt bed is saturated, contains also large amounts of potassium chloride, bromine and boron and can thus be used as an additional source of raw material for the production of boron compounds. Official data covering the production of boron compounds or of boron minerals are not being published. The latter can be estimated at 25,000 to 30,000 tons per year. Boron minerals are not imported anymore."

Historically, borates from countries other than the United States of America have for considerable periods in the past provided the largest source of raw material for the world. In early days Tibet, and later Italy, was the chief source of supply. Then South America took the lead. Since the middle 1920s the great development at Searles Lake and the discovery of the sodium borate deposits at Kramer have pushed the United States to the forefront. Whether this position can be maintained depends on a variety of complex economic conditions that cannot be predicted with accuracy. The United States, as shown in preceding paragraphs, has material competition today from Russia, Italy, Tibet, Turkey and certain South American countries, and recently discoveries have been reported in Iran.

POLITICAL AND COMMERCIAL CONTROL

The origin and mode of occurrence of any deposit is always of interest from a theoretical standpoint. The theory of origin of the borates found in the United States is of commercial and political importance. In 1920, Congress enacted a bill known as the Sodium Leasing Act, which placed in reserve all deposits occurring in public lands in which the sodium content was considered of industrial importance. Such sodium deposits could be mined only through leasing from the Federal Government and by payment of royalties, depending upon the value of the ore removed. At the time of the enactment it was felt that the leasing provision of the bill would not apply to borates, since the boron portion rather than the sodium portion of the mineral was considered to

be the most valuable. However, the Government has maintained that the Sodium Leasing Act applies to any mineral containing sodium. A clause in the Act limited it to sodium "dissolved in and soluble in water, and accumulated by concentration." This clause in effect meant that the origin of a deposit was a deciding factor as to whether or not the deposit could be patented as a placer or lode claim or must be operated under a lease from the United States Government.

Since several claims had been located on Government lands in the Kramer district of Kern County, by different individuals, and since others desired to operate the same claims as a sodium lease, litigation was necessary to decide whether these deposits fell under the Sodium Leasing Act or the General Mining Laws. In 1929, several prominent geologists were heard as witnesses in a suit, among whom were Dr. F. L. Ransom, Hoyt S. Gale, and Dean F. H. Probert, all of whom testified that the sodium borate deposits were formed through replacement of clay shales by sodium borate from deep-seated thermal activity and therefore the sodium borate was not accumulated by superficial concentration. The legal decision allowed the claims to be patented under the General Mining Laws.

In 1928, claims were made on borate deposits through the discovery of a calcium borate in the Kramer district, amounting to 10 acres. Up to the present time no sodium borate has been actually discovered and disclosed in this claim. In 1937, the Land Office of the Department of the Interior, revising an earlier ruling, held that this deposit was a sodium borate deposit and that it should be determined whether the deposit was formed through the accumulation by concentration of sodium borate, or, in other words, whether it was a syngenetic or an epigenetic deposit.

A hearing was held before the Land Department in order that the nature and origin of the borate deposit could be fully determined. Testimony was given in which Dr. J. P. Buwalda and Dr. A. C. Lawson testified, presenting evidence to the effect that borate deposits in the Kramer district were formed through uprising volcanic waters containing sodium borate and the partial replacement of the shales through which these waters passed, along with some deposition of borates. On the other hand, Hoyt S. Gale then testified that in his opinion the deposit was formed through the concentration and deposition of sodium borate from waters flowing into a basin carrying with it mud and silt. Later (October 1946) Mr. Gale published a paper entitled "Geology of the Kramer Borate District, Kern County, California," in the *California Journal of Mines and Geology*, giving a comprehensive report on the geology of the Kramer district. His final conclusion regarding the origin of the sodium borate deposits is that borate salts have been brought from the earth's interior to the surface with volcanic waters and have flowed

over lava beds while they were still hot; that heat from the volcanic waters as well as the heat from the lava beds and exposure to the air rapidly evaporated the water and concentrated solutions of borax were accumulated in pools or lakes that became supersaturated. These lake waters, through a rapid drop in temperature, deposited borax while other salts remained in solution. Through this process borax beds gradually built up and the other soluble salts were removed by overflow of the spent borax solutions.

Theories of Origin

The sodium borate of the Kramer region can generally be described as two layers of different sodium borates interspersed with shale. The lower layer is made of crystals of kernite interbedded with shale and the upper layer consists of borax and interbedded shale. A distinctive feature of the deposit is the total lack of water-soluble salts other than sodium borate. Any theory regarding the genesis of the deposit must account for this total lack of water-soluble salts as well as the formation of two sodium borates—kernite and borax (tincal).

Kernite is sodium borate containing four molecules of water; borax contains ten; furthermore, it is known through phase rule and equilibrium work that under normal pressure kernite can be crystallized only from a water solution when the temperature is above 60°C, and at concentrations that would almost certainly mean borax without any water other than its water of crystallization. Therefore, any theory regarding the origin would have to explain this high concentration of borate solution, high temperature necessary and also that other soluble salts at similar concentrations must have been removed without deposition. In view of all this, it is very difficult to understand the formation of the deposit through the flowing and evaporation of surface waters and the deposition therefrom of kernite.

Another theory, presented by Dr. W. T. Schaller, is that the sodium borate content of the ulexite was dissolved by surface water and carried to a drainage basin and then evaporated to leave behind crystalline borax. This theory accounts for a deposit of sodium borate containing no other soluble salts but this leaching operation requires that two parts of ulexite by weight release approximately one part of borax and leave behind one part of colemanite. Since colemanite is far less soluble than sodium borate, it seems, if this theory is correct, that in the Kramer district there should be far more colemanite in existence than borax, but all exploratory work indicates that this is not true; in fact, there is far more sodium borate in this region than colemanite.

Theories of both Gale and Schaller can explain only the formation of borax, not that of kernite, since the cooling action of evaporation must cause the formation of borax and not the formation of kernite.

However, it has been contended that the heat from a lava intrusion or heat from distortion of the beds may transform the borax to kernite; in other words, it must be contended that borax is the primary mineral and kernite the secondary mineral if the sodium borate was derived from surface waters. At the present time, it is definitely true that the kernite in the lower horizon is slowly changing to borax; that the kernite crystals are very large and the borax crystals small, hence kernite is a primary mineral and borax in the kernite horizon is the secondary mineral. It must be considered that the specific volume of kernite is much less than that of borax, and if kernite was ever formed from borax, there must have occurred a shrinkage of the deposit. There is no such evidence; in fact, the evidence is quite the contrary, showing decided expansion.

The two hypotheses of Schaller and Gale are based upon the need of explaining the absence of salts other than borates, while that of Ranson, Probert, Buwalda, and Lawson is toward the explanation of the existence of the continuous crystals of kernite in the lower horizon, as well as the geological structure of this layer.

The explanation of the lack of other salts can be made only by the assumption that the volcanic waters were saturated with borax and contained no other salts. Such a theory is not true, according to our knowledge of volcanic waters as they occur today, but it should be considered that the sodium borate deposit has no known counterpart in the world and therefore it should be expected that a very unusual condition was the cause of its formation.

Government Leases in the United States

The Leasing Act of 1920 has been amended to omit the clause "dissolved in, and soluble in water and accumulated by concentration," therefore it can be said that in the future any sodium borate cannot be prospected for on Government lands without prospecting permits and cannot be extracted without securing a lease and paying a royalty for the borates extracted.

The borate content of the Searles Lake brine is considered as a sodium borate, therefore the extraction of this sodium borate, if on Government land, can be done only by lease from the Government. At the present time it is probably true that only one third of the brines of Searles Lake are owned in fee while the other two thirds of the brines are on Government lands. Therefore, it appears that in the future the discovery and extraction of sodium borate is greatly dependent upon the policy of the Government, which may vary with changes of administration. Probably any administration will favor the conservation of our natural resources and therefore probably will restrain extraction of sodium borate from Government lands.

PRODUCTION

All figures showing production of borates can be seriously questioned as to accuracy and should be treated rather as rough approximations. As far as world production is concerned, this is obvious, since certain countries do not release such figures for publication; as far as domestic production is concerned, the sources are generally from government and state publications which may be in terms of ore, in terms of borax, in terms of boric oxide, or even in terms of boric acid.

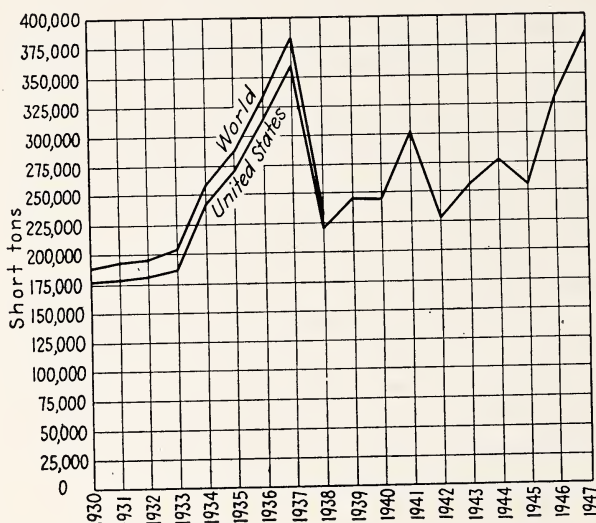


FIG 1—PRODUCTION OF CRUDE BORATES.

Figures for years 1930 to 1940, inclusive, from Mineral Industry; for 1940 to 1941, inclusive, from the Minerals Yearbook, and for 1945 and 1946, from the Division of Mines Report, State of California.

The history of domestic production starts with the first discovery of native borax from lake muds in California in 1864. From 1864 up to the discovery of colemanite (about 1882), the annual production was less than 3000 short tons per year. After the discovery of colemanite, production increased and varied during the next 15 years between 3000 and 8000 short tons per year. From then on, production varied from year to year, until in 1923 it was approximately 125,000 short tons, and eventually it reached a peak of about 350,000 short tons, in 1937. Domestic production from 1930 to 1946 is shown graphically in Fig 1, as well as world production from 1930 to 1938.

PROSPECTING AND EXPLORATION

Solid deposits of borates are generally found underground but occasionally there is evidence through outcropping of calcium borate,

such as colemanite. Generally speaking, it is almost impossible to determine from surface indications the location of borate deposits, although it is almost universally true that these deposits occur in desert regions and where volcanic action is evident. The general method of prospecting is through the assumption that such deposits will occur adjacent to other deposits and, accordingly, most prospecting and exploration is through core drilling near known deposits.

MINING METHODS AND PREPARATION FOR MARKET

At the present time practically the only borates being mined in the United States are in the Kramer district. These deposits are fairly thick and their location varies from 300 to 1000 ft below the surface, the average being about 400 ft. The mining method is that of shrinkage stopping, tramming, and hoisting through vertical shafts to the surface, where the ore is crushed to size suitable for concentration or refining into commercial borax.

A large part of the borax produced in California is from Searles Lake brine, which, besides borax, contains sodium sulphate, sodium carbonate, potassium chloride, and a large percentage of salt.

Two methods are used for recovering the borax from the brine. The first method is that used by the American Potash and Chemical Corporation, wherein the brine is evaporated in triple-effect vacuum pans to remove, in addition to water, salt, sodium carbonate and sodium sulphate. From the resulting concentrated brine, potash is removed by rapid cooling. Finally, borax is crystallized from the solution and refined to commercial borax, which may be sold as such or made anhydrous by fusing in a furnace. Some of the borax is converted into boric acid through the addition of sulphuric acid to a borax solution.

The second method of producing borax from the brine is that used by West End Chemical Co., which consists of the removal of the sodium carbonate portion of the brine through carbonating with carbon dioxide produced from the calcining of limestone. Sodium bicarbonate so formed is removed from the brine and then, by cooling, borax is crystallized out, forming a crude borax. This borax is further refined by dissolving in water and recrystallizing. Pure borax is sold as such or is converted into anhydrous borax in a fusing furnace.

The borate ore mined in Kramer district is essentially 75 pct borax and 25 pct shale. Part of this ore is crushed and shipped to Wilmington (Los Angeles Harbor); there it is dissolved in hot water and the gangue is removed by settling in thickeners. The solution is further clarified by filtration and cooled to crystallize out borax. The remaining mother liquor is recirculated to dissolve more ore. The borax is sold as such, converted into boric acid by treatment with sulphuric acid or fused to make anhydrous borax. Some of the boric acid or borax is converted

into other borates; for instance, potassium borate, ammonium borate, and sodium metaborate.

Another portion of the ore is treated at the mine by crushing and passing over a concentrator to remove about two thirds of the gangue material and then is sold for certain uses or is further concentrated by roasting to remove about one half the water of crystallization. This product contains approximately 45 pct B_2O_3 and in this concentrated form is exported to foreign countries. Another portion of the concentrated ore is completely dehydrated to a glass by fusion and is crushed and sold to industries for which the minor impurities are of no particular concern.

TESTS AND SPECIFICATIONS

The valuable constituent of nearly any borate sold is the boric oxide content and accordingly the only essential specification of the ore is that concerning the boric oxide. The determination of this is made by dissolving a sample in hydrochloric acid, precipitating the interfering elements such as iron and silica by controlled neutralization of the resulting solution, the removal of the precipitate by filtering and, finally, the titration with a standard sodium hydroxide solution of the boric acid content after the addition of mannite or glycerine. The exact procedure ordinarily used is described in Scott's Standard Methods of Chemical Analysis, 5th edition, pages 174-175.

The refined products, borax and boric acid, are of such high purity that it is not necessary to remove impurities before titration. Large quantities of these products are sold as drugs, for which they must conform to the specifications of the U. S. Pharmacopoeia.

MARKETING

Borates, particularly borax, are used in nearly every country in the world. However, the use of these products to any great extent is confined to industrial countries such as the United States, England, France and, before the last war, Germany and Japan. Since the source of borates is largely confined to remote areas such as desert regions and is sold in many countries, the distribution of borates is complex. The problem is involved with the tariffs of various countries as well as with their rate of exchange.

The cost of transportation probably is the largest item of cost in the final marketing of the material. In this country the majority of borax and boric acid is used in areas east of the Mississippi, and the freight charges for transportation amounts to approximately one half of the final cost of the borates. Since the beginning of World War II, ocean freight has doubled or trebled.

USES

Borax is widely used for many purposes. Its easy solubility in water to a mildly alkaline and antiseptic solution, its low melting point and excellent fluxing properties make it one of the most useful of salts. Best known, perhaps, as a household commodity, it is of more importance in manufacturing, and many articles of everyday life require borax in their manufacture.

An excellent cleansing agent, it is widely used in industry and in the home, for washing, cleansing and laundering, either directly or as a constituent of soaps and soap powders.

Borax and boric acid find many applications in medicine and pharmacy, as in disinfectants, mouth washes, tooth powders, cosmetics, lotions, ointments, deodorants and medicated lint and gauze.

Water solutions of borax are used to dissolve casein, which is extensively used in the manufacture of coated papers, playing cards, plywoods, plaster, paints and calcimines. The mild antiseptic character of borax prevents the formation of mold or mildew in starches and sizes, of citrus fruits, leather textiles, etc. It is employed to retard the growth of certain fungi in lumber and for fireproofing wood, paper and fabrics; for neutralizing free acid in leather, and in dyeing leather and textiles. It hastens the cleansing of hides and skins, and boric acid produces a soft, smooth grain in finished leather.

Its use extends to food preservatives, flavoring extracts, syrups and pickles, insect repellents and many others. Almost the whole line of manufacturing products finds use for borax, as in the manufacture of various kinds of implements, candles, carpets, drug specialties, dyes, hats, ink, jewelry, oil, paint, paper, stove polish, tobacco, tools, and many other articles.

Borax and boric acid are essential constituents of porcelain enamels, coating for iron and steel as applied to kitchen utensils, stoves, refrigerators, washing machines, bathtubs, table tops, sinks, signs, pipe lines and an endless array of products requiring an attractive, durable and sanitary finish. The borax also facilitates the addition of coloring pigment to the enamels. In the manufacture of pottery, bricks, china and both white and colored ceramic ware, glazes, and many kinds of glass, borax is indispensable, as it lowers the coefficient of expansion and makes the product more durable. Thus, borax and boric acid give heat-resisting glasses used in the kitchen and laboratory, for lamp chimneys, signal lenses, thermometers and optical glasses. In recent years the glass industry has become one of the largest consumers of borax, as it aids in the melting process and increases the strength, brilliance, and durability of glass.

Borax is a good flux in the brazing, welding, soldering, and so forth

of metals in assaying, in smelting copper and in refining gold and silver. Certain borides are good deoxidizers for nonferrous metal melts, such as brasses and bronzes. Ferroboration in small quantities is a deoxidizer for steel. Boron steels, with less than 0.003 pct boron, are claimed to possess remarkable strength and hardening ability.

Borax glass, calcined borax, and anhydrous boric acid are also useful. Manganese borate is used as a drier in the manufacture of drying oils, linoleum, varnishes, printing and stamping inks. Ammonium borate is used in hair waving and certain types of electrolytic rectifiers and condensers. Boron carbide is extremely hard and is used as an abrasive. Sodium perborate is useful as a disinfectant and solutions of it are used in dyeing and bleaching and in electroplating.

About 10 years ago, a very important use of borates was developed in agriculture. It was discovered that boron is a minor but essential element in the proper growth of all plant life. It has also been found that intensive cropping and tilling of the soil is depleting the boron content of the soil and must be replaced through the addition of borates. Nearly all European countries, as well as many sections in the United States, have discovered this shortage of boron in the soil and, accordingly, are applying borates, either through the addition of borates themselves or through application of fertilizers containing borates.

A peculiar feature in this use is the discovery that an overapplication of borax will have a toxic effect on plant growth. This discovery has been utilized by the agricultural authorities for the control of noxious weeds and in the United States an appreciable amount of borax and concentrated borates is being used for this purpose.

Thus, the cleanser, the pharmacist, the paper and textile manufacturers, the tanner, the potter, the enameler, the glassmaker, the tile-maker, the metallurgist, the brazer, the jeweler, and the farmer all use borax. Hardly any other substance enters into so many diversified lines of manufacture.

PRICE HISTORY

When borax was first produced in California, in 1861, the value of the refined material was 39¢ per pound, and it remained in that neighborhood until 1878, when it dropped to 8 $\frac{7}{8}$ ¢ per pound because of economies in production and, in part, to keener competition among various producers in the United States and to the influence of foreign importation. In 1883, a tariff was placed upon refined borax amounting to 5¢ per pound and 3¢ per pound for crude material. This resulted in an increase in price of 14 $\frac{3}{4}$ ¢ per pound.

From 1883 to 1887, prices were decreased gradually until they reached 5 $\frac{3}{4}$ ¢ per pound, owing to an increased supply of borates mined in California and Nevada. Because of the consolidation of various pro-

ducers in California and an increase in duty of the tariff, in 1890 the price increased to $7\frac{1}{2}\phi$ per pound. However, owing to a reduction of tariff in 1894 and the importation of English refined borax, the price dropped to a low of 5ϕ per pound in 1896. The Dingley Tariff Bill, in 1897, caused the price of refined borax to increase to 7ϕ per pound, where it remained until 1903. From that time the price gradually declined, until in 1913 it dropped to $3\frac{1}{2}\phi$ per pound; then, because of increased freights, labor and production costs, the price increased sharply until it reached a maximum of $8\frac{1}{4}\phi$ per pound. The year 1921 marked a big decline in commodity prices generally, and borax was no exception to this trend.

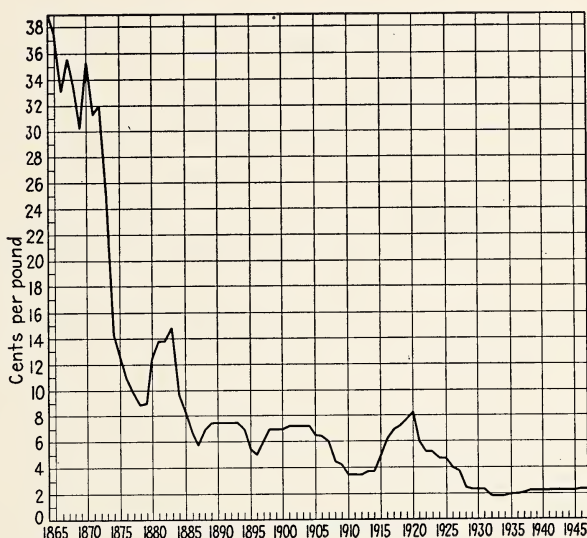


FIG 2—AVERAGE PRICES OF BORAX.

The development of the Searles Lake production exerted undue pressure on prices. The discovery of the Kramer sodium borate mines again had a downward marked influence on prices, which reached an all-time low of approximately $1\frac{1}{5}\phi$ per pound delivered in the east in 1932. Despite great increases in the cost of labor supplies and freights in the past 15 years, prices have risen only about $\frac{1}{2}\phi$ per pound from their all-time lows.

Fig 2 gives the average prices of borax for the years 1864 to 1946 delivered on the Atlantic Coast and in bags.

Price quotations are taken from the following: 1864 to 1871, Bailey;³ 1872 to 1909, The Mineral Industry; 1910 to present time, *Oil Paint and Drug Reporter* (prices of borax per pound, carload lots, gran., New York). From 1864 to 1908, prices are quoted for barrels; from 1909 to the present time, for bags.

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CHAPTER 8

CEMENT MATERIALS

By W. M. MYERS*

THE hydraulic properties exhibited by the calcination products of certain limestones were recognized at an early date—more than 2000 years ago. It was known that calcined limestone with the addition of other minerals would react with water and produce an insoluble and stable product. This material could be cast in desired forms or could be used as a cement for the unification of other materials in large masses or for bonding brick or masonry structures.

Cements are essentially mineral glues and it is their ability to unify other materials plus their fluidity when first mixed with water, enabling the mass to assume any desired shape, that has made them so extraordinarily useful to modern industry. Like other glues, cements do not exhibit their maximum strength when used alone and only when mixed with proper aggregates do their optimum properties appear. The resulting concrete, a mixture of cement, mineral aggregates and frequently of reinforcing steel, exhibits the most desirable properties of the individual constituents with regard to tensile strength, stability and permanence. The speed with which such mixtures can be prepared and installed in place with mechanical equipment has facilitated their adoption by the engineering profession concerned with the construction industries.

The development and application of improved methods of manufacture have resulted in such economies that the finished product can be sold at a remarkably low price. In addition, the necessary raw materials are of such common occurrence and wide geographic distribution that the manufacture of cement was established in 34 of the 48 states by 1946. Plants under construction will add to this number. In recent years the industry has been characterized by the development of a number of new cements designed to possess special properties essential for use in unusual environments. These have introduced the use of some new raw materials and also have complicated the processes of manufacture. In the following pages, the major varieties of cement of commercial importance are treated in the chronological order of their appearance on the market.

* Chief, Division of Mineral Economics, School of Mineral Industries, The Pennsylvania State College, State College, Pennsylvania.

PUZZOLAN CEMENT

Puzzolan cement is one of the oldest cementing materials known. Structures made from it more than 2000 years ago still exist in excellent condition. It was employed extensively by the Roman engineers for many uses. The name is derived from the village of Puzzuoli, Italy, where its most characteristic component, puzzuolana, was quarried. This material is a volcanic ash, the product of igneous activity. It is available in large tonnages and easily extracted. It is a glass exhibiting varying degrees of devitrification, the product of the sudden chilling of molten volcanic rocks. It is widely distributed in Europe and similar products, pumice and pumicite, are abundant in some areas in the United States. In composition, it is essentially a silicate of aluminum, iron, lime, magnesia, and alkalies. Analyses of the hardened cement display wide variations in composition, indicating a lack of uniformity in the raw materials and the absence of any technical control in its manufacture. The cement was prepared by grinding this volcanic ash to a fine powder, and mixing it with quicklime. This mixture was brought to proper consistency with water and used as a mortar in masonry or for construction. These natural glasses possess a low degree of chemical stability and undoubtedly calcium silicates were produced by reaction with the lime. There is a resemblance between the composition of this compound and modern portland cement although it is improbable that the modern cement industry owes any part of its development to this primitive material.

A similar product may be prepared by substituting slag from blast furnaces or other sources for the volcanic glass. Such cements are manufactured in the United States. The quantity is not large, as indicated by the production figures. It is probable that a similar reaction could be obtained using the glass abraded from plate glass during the processes of grinding and polishing. Such material mixed with the sand used as an abrasive exists in large tonnages. The superior qualifications of portland cement and its uniformity have resulted in an almost complete replacement of puzzolan cements. Interest in the puzzolan reaction continues to exist in technical circles and there is little reason to doubt that a cement far superior to the ancient material could be produced under modern management. Considerable interest is in evidence concerning the use of puzzolanas with portland cement. A number of these mixtures are manufactured and it is reported that the U. S. Reclamation Service will try a mixture of the two in a large concrete dam.

NATURAL CEMENTS

Little or no progress was made in the production of mineral cements or in the development of new types until the eighteenth century. It was

recognized then that certain impure limestones, with substantial inclusions of clay and silica that made them unsuitable for the production of lime, could be calcined and that the product of calcination would possess a true hydraulic property; that is, it would set under water and become a hard and permanent mass. These limestones were called hydraulic or "water limes." John Smeaton, an English engineer, is credited with making the discovery in 1756. The investigations he carried on did much to expand knowledge as to the necessary raw materials and their treatment. The Eddystone lighthouse, constructed under his direction on the dangerous shallows off the coast of Cornwall, was a masonry pile bonded with this type of cement. The successful completion of this structure was a significant date in the development of cement and modern lighthouse design. Other workers entered the field and the production of natural cement became a well established industry.

There is little differentiation to be made between the hydraulic limes and natural cement except the temperature of calcination. The usual distinction is whether or not the lump material may be hydrated without grinding to a powder, which is necessary for the natural cement. An increased knowledge of the importance of the presence of alumina and silica led to the use of combinations of materials, and clay or shale was mixed deliberately with limestone, chalk, or other calcareous material to produce the desired composition. The practice later followed in the production of portland cement was thereby fixed in the industry. In general, the processes employed were crude and based on hand labor and the use of water power for grinding the final product. After tests had demonstrated the suitability of the rock for the production of cement, a quarry was opened. The rock was blasted loose in the quarry, broken to desired size, transported to the kilns, and calcined. The kilns were of the vertical type, similar to or adapted slightly from those long in use in the production of lime. Frequently they were built on a sidehill, with an earthen ramp, so that they loaded from the top without direct elevation of the charge. The kiln was filled with alternate layers of coal and rock and ignited. As the charge descended, largely because of the shrinkage caused by the combustion of the fuel, further additions were made at the top. The calcined material, after discharge from the kiln, was crushed and then ground by buhrstones to proper fineness. The buhrstone mill, constructed of opposed disks of selected rock, generally powered by a waterwheel on a stream, is one of the most ancient grinding devices. It was developed for the grinding of grain and adopted by the mineral industries. These mills are still employed in a limited manner for special purposes and products. This primitive kiln and grinding equipment was gradually replaced by more efficient production units.

It is a noteworthy point that the temperatures involved in calcina-

tion are relatively low, being sufficient to disassociate the carbonates and expel the carbon dioxide but not high enough to produce any fusion. In the manufacture of portland cement, kiln temperatures are maintained at a level that will produce some fusion of the clinker. This is the most significant factor separating these two types of cement.

Natural cements were first produced in the United States in 1818, in central New York, where certain horizons of limestone approached an ideal composition for the purpose. The cement produced there played an important role in the masonry construction of the locks that made the Erie Canal a success. The subsequent era of canalization supplied a major market for the material. Present examination of the cement bond in masonry laid 130 years ago shows it to be solid and little damaged by the passage of time. The production of natural cement spread to Pennsylvania, Ohio, Kentucky, Kansas, Wisconsin and other states. Maximum production of record was attained in 1899, when it amounted to 9,868,179 bbl.* By 1911, production was below one million barrels. Subsequent decline has reduced the total to a relatively small figure.

TABLE 1—*Analyses of Magnesian Limestones from Rosendale, N. Y., Used in Manufacture of Natural Cement*^a

Constituent	Composition, Pct				
	1	2	3	4	5
SiO ₂	30.50	29.98	30.84	27.30	27.98
Al ₂ O ₃	6.84	6.88	7.75	7.14	7.28
Fe ₂ O ₃	2.42	2.50	2.11	1.80	1.70
CaCO ₃	34.38	33.23	34.49	35.98	37.59
MgCO ₃	18.00	17.80	17.77	18.00	15.00
Alkalies.....	3.98	7.10	4.00	6.80	7.96
Ignition loss.....	3.78	3.13	3.04	2.98	2.49

^a New York State Museum Bull. 44.

Rosendale, Ulster County, New York, was a prolific producer of natural cement. "Rosendale" became a synonymous expression for natural cements and the term was applied to cements originating in other areas. The proximity of New York city and the use of the Hudson River for transportation aided in the growth of the Ulster County industry. The raw material consisted essentially of an impure high-magnesian limestone. The proportions of silica, alumina, magnesia and

* The cement barrel employed in all domestic statistical data is equivalent to 376 lb, or four 94-lb sacks. The origin of the unit apparently is connected with imports from European sources before the establishment of a domestic industry. These imports arrived in barrels weighing about 400 lb and contained about 376 lb net. The figure was fixed more accurately by the shipment at times of two sacks, each containing 188 lb net of cement to a barrel.

lime, while displaying variation as shown in Table 1, are sufficiently uniform and properly balanced to produce a usable cement. The American Society for Testing Materials specifies performance of natural cements to certain standards but does not specify definite chemical composition. It would be impossible to make portland cement from this rock because of its extremely high magnesia content. Natural cements possess one desirable property, which has enabled them to retain a small market; i.e., plasticity, which serves advantageously in mortar used for laying brick or stone masonry. In this market, natural cements have encountered severe competition from portland cement-lime mortars and especially compounded masonry cements.

PORTLAND CEMENT

Portland cement is the direct descendant of the natural cements of England. It owes its origin to the inventive genius of Joseph Aspdin, 1779–1855, a mason and bricklayer of Leeds, England. In his patent, applied for Dec. 15, 1824, his process is described in the following language:

“My method of making a cement or artificial stone for stuccoing buildings, waterworks, cisterns, or any other purpose to which it may be applicable (and which I call portland cement) is as follows: I take a specific quantity of limestone, such as that generally used for making or repairing roads, and I take it from the roads after it is reduced to a puddle, or powder; but if I cannot procure a sufficient quantity of the above from the roads, I obtain the limestone itself, and I cause the puddle or powder, or the limestone, as the case may be, to be calcined. I then take a specific quantity of argillaceous earth or clay, and mix them with water to a state approaching impalpability, either by manual labour or machinery. After this proceeding I put the above mixture into a slip pan for evaporation, either by the heat of the sun or by submitting it to the action of fire or steam conveyed in flues or pipes under or near the pan until the water is entirely evaporated. Then I break the said mixture into suitable lumps, and calcine them in a furnace similar to a lime kiln till the carbonic acid is entirely expelled. The mixture so calcined is to be ground, beat, or rolled to a fine powder, and is then in a fit state for making cement or artificial stone. This powder is to be mixed with a sufficient quantity of water to bring it into consistency of mortar, and thus applied to the purposes wanted.”

The first cements produced were far inferior to the modern product but decidedly superior to the material previously manufactured. The name “portland” was derived from the resemblance of the set cement to Portland stone, a variety of limestone that is one of the most important building stones in the British Isles.

This stone has been quarried and mined underground for centuries

on Portland Island, on the Dorset coast. It was extensively used by the famed architect, Sir Christopher Wren, in the rebuilding of London after the fire of 1666. Portland stone varies in quality, depending upon the bed from which it has been extracted. Some of the best material is suitable for fine carving and other types are suitable for the production of polished slabs for decorative use. The use of this name for a new product, with its implied resemblance to one of the best and most widely known building materials in the United Kingdom, was a happy choice. At present the term has no significance other than to designate the most widely used modern cement, which is manufactured by a large number of unrelated companies using similar raw materials and processes and producing a similar commodity.

Portland cement of European origin was imported by the United States in increasing amounts after 1860 and the demonstration of its superiority over natural cements of domestic origin resulted in their displacement. The first portland cement manufactured in the United States was made at Coplay, Pennsylvania, in the Lehigh Valley, an area later to become the world's foremost producer. This cement was the result of experimentation carried on by David O. Saylor, of Allentown, a manufacturer of natural cement. Mr. Saylor had noted that the Rosendale-type clinker he was producing showed the greatest strength, when converted to cement and set, when it was burned at a maximum temperature. His investigations proved that mixtures of the local cement rock with high-calcium limestone would produce a cement comparable in performance with that of the imported material.

The first true portland cement, the result of these researches, appeared in 1875. The limestone of the Lehigh Valley is a fortuitous combination of calcium carbonate, clay and silica, low in magnesia, so that it presents nearly an ideal mixture in which the ratios of the principal constituents necessary to make portland cement are present in proper amount. The most marked divergence from a perfect ratio lies in the calcium content which at times and in certain quarries tends to be below the ideal level. This requires the importation of higher-calcium limestones from areas outside the Valley. Knowledge of the industry spread rapidly and cement mills were promptly constructed in other areas, which led to an increased recognition of the fact that other calcareous materials besides cement rock could be employed. The variety of raw materials suitable for the production of portland cement as demonstrated by use increased in number.

RAW MATERIALS IN CEMENT INDUSTRY

Selection of raw materials is controlled by the standards established by the National Bureau of Standards and the American Society for Testing Materials. Chemical composition of the cement must conform

TABLE 2—*Chemical Requirements for Cement*

Constituent	Type I	Type II	Type III	Type IV	Type V
Silicon dioxide (SiO_2), min pct.....		21.0			24.0
Aluminum oxide (Al_2O_3), max pct.....		6.0			4.0
Ferric oxide (Fe_2O_3), max pct.....		6.0		6.5	4.0
Magnesium oxide (MgO), max pct.....	5.0	5.0	5.0	5.0	4.0
Sulphur trioxide (SO_3) max pct.....	2.0	2.0	2.5	2.0	2.0
Loss on ignition, max pct.....	3.0	3.0	3.0	2.3	3.0
Insoluble residue, max pct.....	0.75	0.75	0.75	0.75	0.75
Ratio Al_2O_3 to Fe_2O_3		0.7-2.0			0.7-2.0
Tricalcium silicate ($3\text{CaO} \cdot \text{SiO}_2$) max pct...		50		35	
Dicalcium silicate ($2\text{CaO} \cdot \text{SiO}_2$) min pct....				40	
Tricalcium aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$) max pct.....		8	15	7	5

TABLE 3—*Materials Used in Cement Industry*

Source of CaO	Source of Al_2O_3	Source of SiO_2	Source of Fe
Cement rock	Clay	Clay	Limestones
Limestone	Shale	Shale	Clay
Marl	Ash from coal	Ash	Shale
Fossil shell	Slag	Slag	Iron ores
Recent shell	Igneous rocks	Sand	Slag
Alkali waste		Sandstones	Pyrite cinders
Blast-furnace slag			Mill scale

TABLE 4—*Raw Materials Used in Producing Portland Cement in the United States, 1944-1946^a*
SHORT TONS

Raw Material	1944	1945	1946
Cement rock.....	5,119,318	5,656,390	10,781,078
Limestone.....	19,958,151	22,747,654	34,579,673
Marl.....	643,412	646,391	860,798
Clay and shale.....	2,822,881	3,162,458	4,845,224
Blast-furnace slag.....	278,998	380,970	706,986
Gypsum.....	597,297	683,158	1,157,324
Sand and sandstone.....	230,288	272,077	460,910
Iron materials.....	123,079	128,312	218,634
Miscellaneous.....	22,442	36,100	144,139
Total.....	29,795,866	33,713,510	53,754,766
Average total weight required per barrel (376 lb) of finished cement.....	Pounds 656	Pounds 656	Pounds 655

^a Reported by the U. S. Bureau of Mines.

with the requirements specified or face disqualification in most markets. Proper selection of raw materials in correct proportions, therefore, is essential. The control of these operations is the responsibility of the chemist. The application of chemical control to all processes of cement manufacture has become the most valuable single contributing factor to the remarkable quality and uniformity of the product. The application of chemical control is actually a means to an end of producing a cement with satisfactory physical properties and enduring performance in use.

TABLE 5—Composition of Jacksonburg Cement Rock

Constituent	Composition, Pct	
	1	2
Calcium carbonate (CaCO_3).....	69.00	74.05
Magnesium carbonate (MgCO_3).....	5.70	4.09
Alumina (Al_2O_3).....	5.40	5.19
Iron oxide (Fe_2O_3).....		1.87
Silica (SiO_2).....	19.82	12.66
	99.92	97.86

The American Society for Testing Materials recognizes five types of portland cement:

Type I. For use in general concrete construction when the special properties specified for types II, III, IV, and V are not required.

Type II. For use in general concrete construction exposed to moderate sulphate action or where moderate heat of hydration is required.

Type III. For use when high early strength is required.

Type IV. For use when a low heat of hydration is required.

Type V. For use when high sulphate resistance is required.

Specified composition of these types of cement, which may serve as a guide in the choice of raw materials, is shown in Table 2. Those interested in complete specifications concerning composition of performance and method of testing and analysis should consult the ASTM Standards.²

Materials used in the cement industry are listed in Table 3. In 1944 to 1946, abnormal years because war conditions depressed the construction industries and all markets for cement, the U. S. Bureau of Mines reports distribution of raw material as recorded in Table 4. This table shows the dominant position as measured by tonnage of cement rock and limestone in the raw-material requirements of portland cement.

Cement Rock

Cement rock is a low-magnesium clay containing limestone. The Jacksonburg limestone of the Lehigh Valley is the best known example. In chemical composition, this rock approaches the ideal with regard to lime, alumina, and silica ratios (Table 5). Correction of quarry-run material to desired composition for kiln feed is easily attained by additions of clay or high-calcium limestone.

The occurrence of this material in a densely populated area in large tonnages, near the surface with little overburden, easily quarried and supplying nearly all the constituents necessary for cement, supplied the Lehigh Valley with natural advantages of great economic importance.

Limestones

Limestones are sedimentary rocks deposited in shallow sea waters. They are composed essentially of calcium carbonate and varying percentages of magnesium carbonate and mechanically admixed impurities of clay and sand. Clay and sand are no longer objectionable impurities when the rock is used for the manufacture of portland cement. They supply the alumina, silica, and iron oxide necessary for the formation of the desired silicates in the cement. Limestones are formed by the precipitation of calcium carbonate from solution or more commonly by the accumulation and lithification of fragments of calcareous material that originally was secreted from water by living organisms. Limestones with a purity above 99 pct calcium carbonate are exceedingly rare. Many accessory minerals may be present, including iron and manganese oxides, sulphides of the common metals, authigenic feldspars, mica, gypsum, celestite, fluorite, and bituminous matter. They vary greatly in texture and color. Exposed surfaces commonly weather to a pale gray or buff but the same rock on a freshly fractured surface may be black.

Limestone is used as a term to include all carbonate rocks containing appreciable quantities of calcium, of which dolomite, a carbonate of calcium and magnesium, is one. Because of its high magnesium content, dolomite cannot be used for the production of portland cement. It can be distinguished readily in the field by the use of dilute hydrochloric acid, in which it dissolves slowly with little or no effervescence. Calcium limestones dissolve rapidly with vigorous effervescence. Limestones frequently exhibit considerable variation in composition from layer to layer. The effect of such variations may be neutralized by operation of the quarry in such a manner as to average variables and produce a uniform kiln feed. Limestones possess a characteristic common to other

sediments deposited in stratigraphic succession—they may change completely in composition if followed laterally for miles. The gradual increase in silica content is so great that instances are known of a limestone horizon displaying every gradation from a fairly pure carbonate rock to a sandstone.

Limestones were formed originally in nearly horizontal layers but owing to changes in the earth's crust, and at times intense folding and faulting, they are found now in a great variety of attitudes. Such structures may be so complex as to introduce difficult problems in quarry operation. Such geologic processes have been carried on at times in the geologic past to such extremes as to produce temperatures and pressures sufficient to recrystallize the limestone and produce its metamorphic equivalent, marble. Impurities in the rock are also metamorphosed, producing a new suite of accessory minerals in which the silicates predominate.

The most important factor controlling the suitability of limestone for the manufacture of portland cement is its magnesium oxide content. As shown in Table 2, the maximum content permissible is 5 pct in the finished cement. Owing to the relative increase of the magnesium oxide content in the clinker as compared with the raw materials, caused by the elimination of carbon dioxide during calcination, the limestone would contain less than 3 pct. Such limestones are by no means common, as any geologist knows who has engaged in the search for raw materials suitable for the cement industry—many limestones, widely distributed and occurring in billions of tons, contain too much magnesia to qualify. The geographic location of the cement industry has been affected by this specification. Next to magnesia, silica and alumina may become the most influential impurities. If occurring in too high a percentage, their presence must be corrected by the introduction of pure high-calcium limestones from outside sources, introducing an additional item of cost. The introduction of the flotation process has facilitated the elimination of silica and made possible the utilization of limestones otherwise not suitable.

Marls and Shell Marls

Marls are earthy, friable accumulations of calcareous material secreted by plants and animals in lakes and marshes. Over long periods of time the skeletal remains of plants mixed with shells of animals may form beds as much as 30 ft thick, containing substantial tonnages of material suitable for cement manufacture, but such deposits are not common. They are noted at times in areas where the saturation of ground water with calcium carbonate permits the growth of algae, producing the common blue-green coloration of springs where ground

water emerges at the surface. As a raw material for cement manufacture, they are important in Michigan. The glacial drift of the area contains limestone pebbles and ground limestone in quantity. Solution of this material in meteoric waters has supplied the lime necessary for the growth of organic life, which has flourished in the numerous shallow lakes of the area. The death of countless generations of these organisms and the accumulation of their limy residues has produced thousands of tons of commercial material, which is dug from dried marshes or dredged from ponds. Mixed with clay available in the immediate vicinity, it forms a suitable mix for kiln feed. In analysis, these marls frequently run over 90 pct calcium carbonate and 2 to 3 pct magnesium carbonate with small amounts of silica, alumina and iron. The importance of marl as a raw material has declined because of the exhaustion of readily accessible deposits.

Shell marls exist in tonnage along the coasts of Virginia and North and South Carolina. They consist of mixtures of fossil shells, shell fragments and varying amounts of clay and sand accumulated during Tertiary time. The magnesia content is low and the clay and sand content serves to supply part of the requirements of silica and alumina. The rest is obtained from clay deposits present near the cement mill. The marls occur in flat-lying beds, up to 20 ft thick, with a thin overburden. The material is dredged and transported by barge to the mill. The use of water transportation is an economic aid.

Other Cement-making Materials

Recent Shells—Oyster and clam shells of recent origin have been collected and burned for lime from Nova Scotia to Texas. Some of the collections of shell were formed by Indians in pre-Columbian time. Tonnage adequate for cement manufacture is not known on the Atlantic Coast; in California, on the west side of San Francisco Bay, such shells occur in deposits as much as 30 ft thick. They have been found suitable for cement manufacture. Oyster shells are also the principal source of lime for the cement manufacturers at Houston, Texas.

Chalk—Chalk, a soft, friable form of calcium carbonate of high purity, has been used for cement manufacture in England, France, and Belgium, where it occurs abundantly. It is found in deposits formed during Cretaceous time. Chalk occurs in some areas in the United States and has been employed as a cement material in Alabama and Arkansas.

Alkali Waste—Limestones are quarried in large tonnages as a source of carbon dioxide to be combined with sodium chloride in the manufacture of sodium carbonate. A waste by-product of the process is precipitated calcium carbonate. This material is not suitable for use

as an original source of carbon dioxide and therefore is rejected as a waste product. The tonnage accumulated from years of activity plus current output is sufficient to qualify it as a raw material for cement manufacture.

Blast-furnace Slag—Basic blast-furnace slag may be substituted in part for the raw materials used in the production of portland cement. Where the slag is so employed it is desirable that the fluxing stone charged to the furnace be a high-calcium limestone and not a dolomite, with its objectional magnesium content. The cement is identical with other portlands, as the slag is mixed with limestone and serves to introduce a part of the lime, silica, alumina, and iron oxide, which otherwise would be derived from other sources.

Clay and Shale—Where alumina and silica are not present in the limestone in proper amounts, and this is true for operations other than those concerned with cement rock, it is necessary to use clay or shale. There is little difference in chemical composition between the two materials. Clay is an earthy, easily disintegrated, widely distributed mineral; shales are composed of clay minerals deposited in water in thin layers and subjected to some pressure and cementation, with some lithification. Shales are weak rocks but do not disintegrate as readily as the unconsolidated clays and therefore require grinding. Both clays and shales display wide variations in mineralogical and chemical content; some consist essentially of aluminum silicates, others may contain more than 50 pct free silica. Adjustment of the silica content may be necessary. Grain size is important and very finely divided silica is to be preferred.

Sand and Sandstones—Where a silica deficiency exists it may be corrected by using sand or sandstones. These materials are chiefly quartz in content but may contain varying amounts of clay and other minerals. The tonnage used is comparatively small, as shown in Table 3.

Iron Materials—The development of cements with a low heat of hydration has created a demand for high-iron raw material. Those commonly used are iron ores, pyrite cinder, the product of the calcination of pyrite, and mill scale, the product of the hot-handling ingot, billets and other forms of steel. All common portland cements contain some iron and the addition of materials listed above is designed to produce a cement of exceptional performance.

Miscellaneous—Most of the miscellaneous products in addition to gypsum are introduced in the cement after the clinker has been manufactured, to secure special effects. Among those listed are diatomite, pumice, flue dust, hydrated lime, tufa, cinders, calcium chloride, tannic acid, grinding aids and air-entraining compounds.

Distribution of production according to raw material is shown in Table 6.

Gypsum

The role of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is so extraordinary that it deserves special mention. It is added to the clinker before the final operation of fine grinding to the finished cement. The amount added is controlled by the specification for cement, which for most types is fixed at a maximum of 2 pct SO_3 . As the clinker may contain from 0.25 to 0.50 pct SO_3 , mostly derived from the fuel, the amount of gypsum added must be adjusted accordingly. Each barrel of cement generally requires from 9 to 12 lb of gypsum. In the aggregate the total requirements of the country total a large figure and in some years over one million tons of gypsum have been consumed in this market.

TABLE 6—*Production and Percentage of Total Output of Portland Cement in the United States, According to Raw Materials^a*

Year	Cement Rock and Pure Limestone		Limestone and Clay or Shale		Marl and Clay		Blast-furnace Slag and Limestone	
	Bbl	Pct	Bbl	Pct	Bbl	Pct	Bbl	Pct
1941.	46,534,193	28.4	102,285,699 ^b	62.3	3,142,021	1.9	12,068,646	7.4
1942.	49,479,304	27.0	115,948,373 ^b	63.4	3,009,562	1.7	14,343,945	7.9
1943.	29,915,157	22.4	92,310,018 ^b	69.2	2,300,636	1.7	8,897,977	6.7
1944.	17,609,035	19.4	65,478,178 ^b	72.0	2,078,530	2.3	5,739,933	6.3
1945.	20,383,505	19.8	73,409,831 ^b	71.4	2,035,236	2.0	6,976,312	6.8
1946.	39,070,643	23.8	112,142,154 ^b	68.4	2,720,500	1.7	10,130,891	6.2

^a Data from U. S. Bureau of Mines.

^b Includes output of plants using oyster shells and clay.

Gypsum serves as an additional safeguard in controlling the set of the cement. It prevents a quick set and ensures the delivery of a uniform and dependable material. This is one of the most desirable features possessed by portland cement and perhaps nothing has done more to establish this material in industry than dependability of performance. Plaster of paris, a form of calcined gypsum, was first utilized for this purpose in Germany. It was used for a time in the United States and then replaced by the more economical rock gypsum. As gypsum decomposes to form plaster of paris at a low temperature, it is probable that much of the material is so converted by the temperatures attained by grinding clinker. Gypsum for this purpose is mined in many states. It is generally a product of gypsum quarrying or mining operations carried on incident to the manufacture of plaster of paris in its multiple forms. Cement mills near the Atlantic seaboard are supplied in part by imports from Nova Scotia. Gypsum production in this area is located near tidewater and can be laid down reasonably at Atlantic ports.

Gypsum contains 46.6 pct SO_3 ; anhydrite, CaSO_4 , contains 58.8

pct SO_3 . Anhydrite occurs in large tonnages, associated with gypsum in many localities. Its use as a substitute for gypsum has been the subject of research.³¹ It has little value for any other purpose except in the field of agriculture. In Europe it has been used as a source of lime in the manufacture of cement. Gypsum-anhydrite mixtures containing up to 50 pct anhydrite have been used for retarding the set of cement. The advisability of employing pure anhydrite is still the subject of debate.

Gypsum produced as a by-product in the phosphate baking-powder industry and from other sources has been used in place of rock gypsum.

Fuels

The choice of fuel is based on economic considerations and solid, liquid and gaseous fuels are used. Bituminous coal is by far the most important and more than half of the cement manufactured in the United States is prepared with this fuel. Small quantities of anthracite have been employed in eastern Pennsylvania with bituminous coal. This fuel ignites slowly and tends to burn at the end of the flame, thereby increasing its length. Cement companies seldom own their own sources of fuel. They buy it in the open market and generally it is the major item purchased for operation as measured by dollar expenditure. The relationship of quantity of cement to fuel consumed is shown in Table 7.

ECONOMICS OF THE INDUSTRY

Capital is a basic necessity. It is doubtful, except under the most exceptional circumstances, that a cement mill would be built today with an annual capacity less than 600,000 bbl. As such a mill could scarcely be built for much less than \$4.50 per annual barrel, it is evident that cementmaking is a major industry, which cannot be initiated without substantial financial resources.

Basic data relative to the magnitude of the industry in the United States are listed in Table 8. It is evident that the realization per barrel of cement at the factory is extraordinarily low when the amount of capital and the tonnage of raw material is considered. The largest and most recently constructed mills tend to be the most efficient and most competent to produce quality cement from refractory materials. The productive capacity is greatly in excess of demand and seldom is utilized beyond two thirds of the total rating. Inducement to engage in the industry is limited, therefore, except under exceptional circumstances and is not attractive except in areas in which the markets are not already saturated by competitive production.

The location of the industry is controlled by the raw materials, which generally are within short distances from any one central

TABLE 7—*Portland Cement Produced in the United States, 1946, by Kinds of Fuel^a*

Fuel	Finished Cement Produced			Fuel Consumed ^b		
	Number of Plants	Barrels of 376 Pounds	Percentage of Total	Coal, Short Tons	Oil, Barrels of 42 Gallons	Natural Gas, M Cu Ft
Coal.....	91	92,469,773 ^c	56.3	5,746,785		
Oil.....	13	12,615,568 ^c	7.7		2,583,183	
Natural gas.....	12	11,762,138 ^c	7.2			17,397,628
Coal and oil.....	10	14,566,471	8.9	883,015	554,919	
Coal and natural gas.....	13	13,281,081	8.1	359,160		16,025,258 ^d
Oil and natural gas.....	7	13,324,422	8.1		764,048	15,034,902
Coal, oil, and natural gas.....	6	6,044,735	3.7	19,770	84,271	9,546,321
	152	164,064,188	100.0	7,008,730 ^e	3,986,421	58,004,109

^a Reported by U. S. Bureau of Mines.^b Figures compiled from monthly estimates of the producers.^c Average consumption of fuel per barrel of cement produced was as follows: 1945—Coal, 126.9 lb; oil, 0.2041 bbl; natural gas, 1,421 cu ft. 1946—Coal, 124.3 lb; oil, 0.2048 bbl; natural gas, 1,479 cu ft.^d Includes 2,090,100 M cu ft of byproduct gas.^e Includes 19,120 tons of anthracite, and 6,989,610 tons of bituminous coal.TABLE 8—*Production and Price of Portland Cement and Capacity Utilized*

Year	Barrels Produced	Average Factory Price per Barrel	Percentage of Capacity Utilized
1936.....	112,649,782	\$1.51	44.1
1937.....	116,174,708	1.48	45.5
1938.....	105,357,000	1.45	41.2
1939.....	122,259,154	1.47	47.7
1940.....	130,216,511	1.46	51.2
1941.....	164,030,559	1.47	66.3
1942.....	182,781,184	1.53	73.5
1943.....	133,423,788	1.57	55.0
1944.....	90,905,696	1.59	37.8
1945.....	102,804,884	1.63	42.5
1946.....	164,064,188	1.72	67.9
1947.....	186,519,347	1.90	74.9

point that can be used for a mill. As either limestone or cement rock is the largest tonnage item to be considered, it is common practice to build the mill at the quarry and introduce shale, clay, fuel and gypsum from the nearest sources. Notable exceptions to this custom are the cement mills fringing the Great Lakes. Cheap transportation by water

permits the shipment of limestone to these mills from relatively distant quarries. A similar condition exists in Alabama, Louisiana, and Washington.

Of all the materials used in large quantities, gypsum travels the greatest distance, owing to the economy with which it can be moved on water, either on the Atlantic moving southward from Canada to the eastern seaboard or on the Pacific moving northward from Mexico to the west coast.

A few by-products may be sold, such as lime, crushed stone and building stone, and small amounts of potash, but with few exceptions the cement industry presents a picture of a large investment aimed at the production of a single product. Interference with the market for this product cripples the entire operation. Interference with production during the war years, when the construction industries were at a low level, led to attempts to divert idle equipment, which is of such a special nature that little use could be found for it except for the production of lime, the defluorinating of phosphate rock and similar calcining operations.

The cement industry is concerned with one remarkable waste of a mineral product; that is, carbon dioxide produced in the calcination of carbonate rocks plus additions from the combustion of the fuel. Hundreds of tons a day may be produced at a single location. The gas is dilute and contaminated with undesirable impurities and interest in commercial recovery is restricted by the limited markets for the commodity. Recovery, purification and compression of carbon dioxide into dry ice is now practiced at one cement mill in Oklahoma.

DISTRIBUTION AND POLITICAL AND COMMERCIAL CONTROL

Distribution of the materials used in the production of portland cement is worldwide. As mentioned before, it is not the rarity of the raw materials but the necessity for assembling in one area the minerals and fuels that cooperatively act to produce cement that controls the location of the industry. As noted, cement is produced in many states, whose number will be increased by the completion of mills now under construction. Germany, Russia, Japan, Italy, are substantial producers. Production in South America is increasing rapidly.

The lowering of duties by the United States will encourage imports. Sea-coast plants in Great Britain, Denmark, Holland, Belgium, Germany, France, and Japan are in a favorable position. Future imports may well be substantially greater than those recorded in the past. Exports normally do not exceed two million barrels. In 1945, more than six million barrels was exported, largely to Mexico and South America. Markets south of the border are increasing in spite of a growing productive capacity in the southern republics.

PROSPECTING AND EXPLORATION

As mentioned before, the chemical requirements of rock suitable for the manufacture are rigid and comparatively few limestones can qualify. In addition, proper sources of alumina and silica must be found within a short distance and satisfactory fuels must be available. All of these commodities must be located in an area containing a population capable of absorbing the cement produced and not dominated by existing production. The problem as to where to prospect, therefore, is as much economic as geologic.

Stratigraphy is a division of geology concerned with the formation, composition, sequence, and correlation of sedimentary rocks, including limestone. A geologist specializing in stratigraphy is equipped to deal with the basic problem as to what general areas might be expected to contain correct materials. A study of the rock structures and the application of data derived from fossils and heavy mineral residues may make it possible to correlate areas of known qualifications with others of potential but unknown value.

Possibly the greatest service of the geologist at this stage of exploration is not to designate where to drill but to state where not to, thereby preventing the waste of exploration funds in hopeless areas. In an area of definite promise the first consideration is the depth of the overburden. This may be so excessive as to introduce an extra cost item of such magnitude as to exclude the ground from consideration. The overburden may contain the clay necessary for the mix and thereby contribute to the enterprise. Determination of the extent and the chemical composition of the overburden and the possibility of its use must be made. Surface exposures of limestone differ in composition with the bulk of the material found at greater depth, owing to differential solution of the rock by rain water. Surface sampling may introduce error. A similar condition exists at the contact between the rock and a soil overburden. Solution at this point by ground water removes the most soluble constituents of the limestone and the residual material frequently will be found nonrepresentative of the underlying rock.

As limestone may vary widely in composition from strata to strata, a collection of truly representative samples must be made to estimate the average run of material that might be obtained by mine or quarry operation. The difficulty of this operation may be increased by the displacement of the limestone beds from their original horizontal position. The beds may be contorted in intricate form or overturned so that they are standing at a 90° angle, therefore sampling may become a matter of lateral rather than vertical progression.

Surface trenching is the simplest manner of sampling and in areas of great and known uniformity of the rock structure may serve. Gen-

erally it is necessary to take samples to greater depth and drilling must be employed. Well drills have been used with satisfaction in flat-lying rocks in simple geologic structures. The drill cuttings and sludges may be collected over short intervals and analyzed to determine composition. Contamination of the samples by introduction of rock falling in from higher levels in the drill hole is possible. The validity of the sample may be destroyed by the introduction of clay from seams in the rock or the loss of suitable material where the rock is soft, easily crushed and lost with the drill water. Close observation of the drilling operations is necessary.

The diamond drill is the most satisfactory tool for the exploration of most deposits. Its use permits the extraction of a core of rock for examination and chemical analysis. The cores are generally one inch or greater in diameter and at times their study will permit an accurate reconstruction of the geologic structures penetrated by the drill. The percentage of recovery of core is important and at times may fall to a low percentage of the rock traversed. Solid, unaltered rock may permit 100 pct recovery, a condition not commonly attained. Rock that has been decomposed by solution, introduction of clay seams or mechanical shattering may be drillable only with difficulty and the core recovery may fall below 50 pct. Skill in operation of the drill and interpretation of the results is requisite.

Modern quarry operation has been so mechanized that little selection of the rock can be made, a procedure that was possible in the days of hand loading. The selection of a quarry face in which the average of all the strata encountered will qualify for kiln feed is necessary. Other raw materials, clay, shale, or sandstone, may be sampled by similar methods.

In addition to exploration for quality, attention must be paid to quantity. A successful operation can be predicted only where exploration has proved the existence of sufficient tonnage of material to allow operation of the mill for enough years to amortize the original investment and provide a satisfactory return. Capital cannot be interested in the construction of a cement mill until the exploration of the deposit has been completed and tonnage proved by drilling.

MINING METHODS

The quarrying methods employed in the production of rock for cement manufacture have been reported in an extensive literature devoted to the subject. They are similar to the methods employed in the production of crushed stone. The methods adopted for an individual operation are those most suitable to cope with local conditions, which vary enormously. The principal problem encountered in quarrying frequently is to obtain rock of varying composition from a number of

working faces in such a manner as to produce a uniform product with an average composition suitable for blending with other raw materials for the kiln. Common practice is to employ churn drills back of the quarry face. Holes are spaced from the face and from each other at distances most efficient for breaking the rock as determined by experience. The drill holes may be sprung, enlarged at the base, to permit the use of large amounts of explosive, or may be loaded without enlargement of the diameter. After the holes are shot, excessively large blocks of rock may be reduced by secondary blasting to a size permitting loading by power shovel to cars or trucks.

The extraction of limestone by underground mining tends to increase, frequently because the depth or width of the quarry becomes too great for operation or in order to follow dipping strata with a constantly increasing depth of overburden. Mining offers certain advantages: (1) removal of overburden is not necessary, (2) interference by changes in the weather is not serious, (3) the fine stone is clean and free from mud introduced from the overburden by rain or frost, (4) the mine can be worked in areas where the dust and blasting disturbance of a quarry would not be tolerated. Production of rock from a mine tends to be more expensive than quarrying and problems of ventilation, falling rock, excessive fines, and transportation to the surface must be solved.

PREPARATION FOR MARKET

The limestone or its calcareous equivalent must be crushed, transported to storage, and prepared for proportioning with other raw materials. Proportioning consists of mixing the raw materials in quantities designed to produce a clinker of desired composition. The entire operation is conducted under exact chemical control and the calculation of the correct proportions has been the subject of great study.³⁵ After blending, the raw materials are ground to a fine state, so that the desired reactions in the kiln may be completed without the use of excessively high temperatures. Grinding is done both wet and dry. Wet grinding contributes to the uniformity of the product but results in a wet pulp, which must be dried in the kiln, and thus increases fuel consumption. More than half the total quantity of portland cement manufactured is the product of wet mills.

The rotary kiln was first introduced in America in 1886. Probably it is the largest single unit of moving machinery. The tendency has been to increase the length of the kiln in the interests of fuel economy and a single kiln up to 500 ft or more in length is utilized. The kiln is a cylindrical tube of steel lined with brick and proper refractories. It is revolved very slowly and, as it lies on a slight incline, the charge gradually moves to the lowest end, where the burning equipment is placed.

As the charge moves down the kiln, it is heated enough to expel the moisture, free and combined; then the carbonates are broken down and the carbon dioxide is expelled. The oxides then react with the silica and complex silicates and aluminates are formed. Near the discharge end the temperature is sufficient to produce partial fusion.

The clinker produced is very stable. It may be stored under water or in the open without injury or even with some improvement due to the hydration of any free lime present. The chemical composition of clinker is known with accuracy because of its frequent analysis in the laboratory. The actual compounds or synthetic minerals occurring in clinker have been the subject of protracted research and their identity is not yet established entirely satisfactorily. Tricalcium silicate is possibly the most important constituent, followed by dicalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite. In the final operation in the manufacture of cement, the clinker is mixed with the correct amount of gypsum to produce the desired percentage of SO_3 and is ground to specified fineness. From this time to its final disposition, the cement must be protected from moisture or water in any form. Its hydraulic properties are fully developed and the addition of water to the cement produces the final reactions that cause setting. The activity of the ground cement is due to its great surface exposure induced by fine grinding.

In addition to the five types of portland cement described, other special cements are produced in smaller quantities: masonry cement, with high plasticity; waterproof cement, including various waterproofing compounds; and white cement are prepared for special markets. The effects produced by the inclusion of small percentages of air bubbles were observed around 1937, which led to the marketing of special cements known as air-entraining cements. The process is most commonly applied to Type I and Type II cements. A number of special reagents have been prepared to produce the bubbles; Vinsol resin and Darex, tradenames for such reagents, have been employed extensively. Air-entraining cements have been found to be particularly suitable for use in areas exposed to severe frost. The presence of the minute, evenly distributed air bubbles induced by the presence of the air-entraining compound throughout the concrete increases workability and the resistance of the concrete to scaling caused by alternate freezing and thawing.

The Flotation Process

The flotation process as first used for the improvement of metallic ores consisted in adding oils to the ground ore, which was then agitated in water. The heavy sulphides containing the valuable metals became coated with heavy oil and floated to the surface on a froth produced by

the addition of other oils to the moving water. The ordinary processes of separation were thereby reversed, the heavy minerals went to the surface and the lighter dropped to the bottom. The process could be operated continuously and the heavy minerals removed for shipment or direct charge to the smelter. The lighter minerals went to the waste pile. From this crude beginning, the flotation process has been altered and

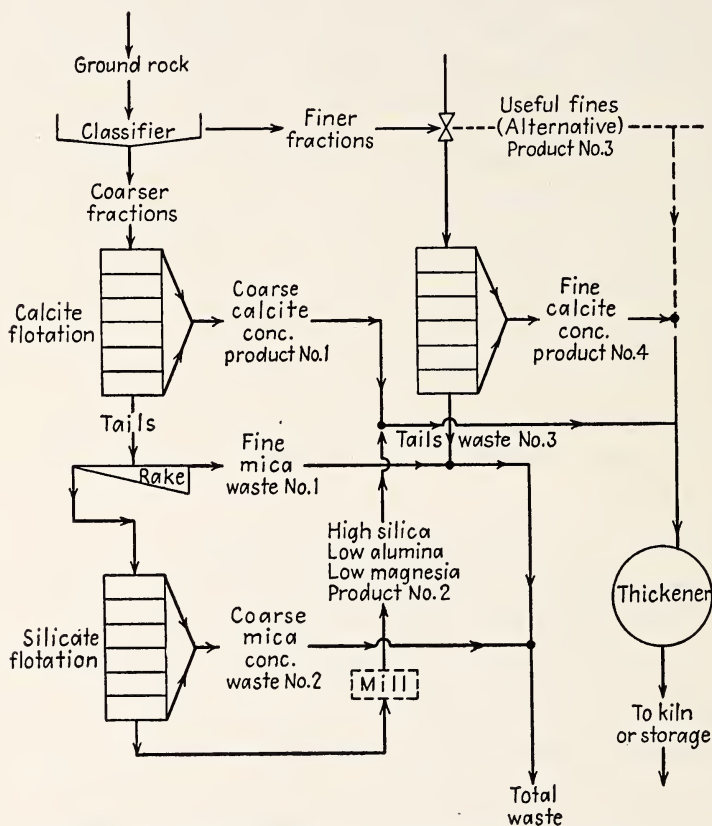


FIG 1—FLOWSHEET OF SEPARATION PLANT OF VALLEY FORGE CEMENT COMPANY.

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improved by research until it has become an exact science applicable to many minerals other than those mined for the production of metal. A large number of special reagents, employed in an acid or alkaline circuit, have replaced largely the oils used at first for collectors and complex ores may be so treated as to permit the recovery of all the valuable components present.

The process was applied to the improvement of limestone for the first time by the Valley Forge Cement Co., of West Conshohocken, Pennsylvania: It is reported that since March 15, 1934, all the cement manufactured at that plant has been made with the aid of the flotation

process.¹² The use of the process has been adopted by other mills in Pennsylvania³³ and has been successful in a number of foreign countries. Perhaps its greatest asset is that it permits the use of rock excessively high in silica and silicates. Engelhart¹² states that its use permits the manufacture of portland cement of the highest quality and in the various modern types from materials previously considered inferior and useless in manufacture of cement. This has permitted the erection of mills near markets and brought about a great saving in the delivered cost of the product. Flotation cells can be installed without great inconvenience in a wet-grinding mill. The initial cost and operating costs are the only liabilities. There is a saving in cost of handling rock at the quarry, as selection of the rock is not necessary. There is some additional saving in fuel and clinker-grinding costs. The flowsheet of the Valley Forge Cement Co. as reported by Engelhart¹² is represented by Fig 1. The presence of mica in this limestone is an unusual mineral association.

MARKETING AND USES

Consumers of large quantities of cement—for instance, the Government—buy directly from the producer on a contract price. Users of smaller amounts buy from local dealers, who stock the commodity for the convenience of the locality and will sell as small a quantity as a single bag. The industry is highly competitive in many localities where there are a number of mills within shipping radius, therefore attempts are made to establish brand preferences among consumers. A substantial item in selling costs is transportation charge. Distribution of shipments by carrier and type of container are given in Table 9.

TABLE 9—Shipments of Portland Cement from Mills in the United States (Including Puerto Rico), 1946, by Types of Carriers^a

BARRELS OF 376 POUNDS

Type of Carrier ^b	In Bulk		In Containers				Total Shipments	
			Bags		Other Containers ^d	Total		
			Paper	Cloth				
Truck.....	10,466,492 ^c	20.7	14,987,432	3,830,531		18,817,963	29,284,455	17.3
Railroad.....	38,586,917	76.3	75,889,354	22,996,350	13,967	98,899,671	137,486,588	81.1
Boat.....	1,521,447	3.0	1,142,487	132,616		1,275,103	2,796,550	1.6
	50,574,856	100.0	92,019,273	26,959,497	13,967	118,992,737	169,567,593	100.0
Percentage of total.....	29.8		54.3	15.9	^e	70.2	100.0	

^a Reported by the U. S. Bureau of Mines.

^b Includes mill in Hawaii; product shipped in paper bags by truck and railroad in 1945 and by truck only in 1946.

^c Includes cement used at mills by producers as follows—1946: 584,224 barrels.

^d Includes steel drums and iron and wood barrels.

^e Less than 0.05 pct.

The uses of cement are almost unlimited. It can be substituted at times for wood, steel, brick, or masonry. The use of this fluid stone has made heavy masonry obsolete except for special purposes. New uses constantly appear and in the aggregate add appreciably to the market for this material.

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CHAPTER 9

CHALK AND WHITING*

BY HEWITT WILSON†

CHALK is soft, pulverulent limestone formed from calcareous remains of microscopic organisms. Whiting is the powder made by the fine-grinding of limestone. Although European chalk dominated the early American market and is still shipped to the eastern and western seaboard, the domestic producer, by new technical processing, improved equipment, and proper selection and mixing of raw materials has shown that the United States can be independent of foreign sources.

DISTRIBUTION

European Chalk—Outcrops of Cretaceous chalk are found in the area roughly bounded by Antrim, Ireland, on the east, East Prussia on the west, Sweden and Scotland on the north, and Nice, France, on the south. Commercial chalk is mined from the chalk cliffs between Dover and Hull, England; from deposits near Mons, in the Departments of Pas de Calais and Nord in northern France; and from similar deposits in Denmark and Belgium.

United States—Some grade of limestone is found in every state of the Union, but true chalk of Cretaceous age is limited to three large areas in the central and southern states. Niobrara (Cretaceous) chalk outcrops are found as a narrow band encircling the Black Hills in South Dakota, Wyoming, and Nebraska, and in much larger exposures in southeastern South Dakota, eastern Nebraska, and western Kansas. A third chalk belt extends from west central Arkansas into Oklahoma and connects with the Austin beds, which almost cross Texas. In the southeastern states, the Selma chalk extends from western Tennessee south through northern Mississippi and turns east across central Alabama.

Most of the domestic chalks are discolored with iron oxide or carbon. Some marls can be included with chalks of commercial possibilities. Some of the soft, cream-colored limestones of northern Florida, Georgia,

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† Supervising Engineer, Electrotechnical Laboratory, Bureau of Mines, Norris, Tennessee.

Alabama and probably Mississippi, Louisiana, and South Carolina, are similar to chalk in original hardness, particle size, and working properties but have a different origin.

ORIGIN AND MODE OF OCCURRENCE

Although the remains of echinoids, mollusks, corals, sponges, and even vertebrate animals are included as fossils in chalk deposits and are of primary importance in faunal and stratigraphic studies, they are secondary in importance to the microskeletons of coccolithophores and rhabdoliths that constitute the larger part of the chalk. These are plant organisms that secrete a number of calcareous disks (coccoliths) or trumpet-shaped bodies (rhabdoliths) on their surfaces, and when they die their calcareous remains mingle with precipitated calcium carbonate and the remains of foraminifera and other organisms that form an important part of deep-sea deposits.

COMMERCIAL CONTROL

European chalks have light cream and gray colors near white, natural plasticity, fineness of grain, and are easily prepared by simple grinding and classification. The water transportation to the eastern seaboard is also comparatively cheap.

With the exception of a few American chalks from Arkansas, Kansas, and Texas, from which putty has been made, domestic chalks have been used commercially only for portland cement and lime. The domestic chalks have the fine particle size of the European chalks, a similar paleontological origin, and an even stronger putty plasticity, but a study by the U. S. Bureau of Mines indicated that the domestic materials did not equal the European in color and purity. Their occurrence is so widespread that better colored deposits undoubtedly will be found in the future. As black, gray, cream and brown colors are not a handicap in certain putty, rubber and other products, it is believed that the domestic chalks could be useful where their fine particle size and plasticity are desirable.

Certain limestones of Illinois, Missouri, and Pennsylvania develop good plasticity with proper grinding treatment, and some of these have better color than the European chalks. The fortification of weakly plastic limestones and marbles with European chalks is practiced to a limited extent, especially along the Atlantic coast. Shell from the coastal waters is often found in sufficient quantities for addition as a plasticizer.

Some of the golden-brown chalks of South Dakota, Kansas, Arkansas, and Texas have colors similar to ochers and siennas and when diluted produce creams of desirable hues. The darkest Alabama chalks give a "driftwood"-gray pigment on dilution, as in a paint extender.

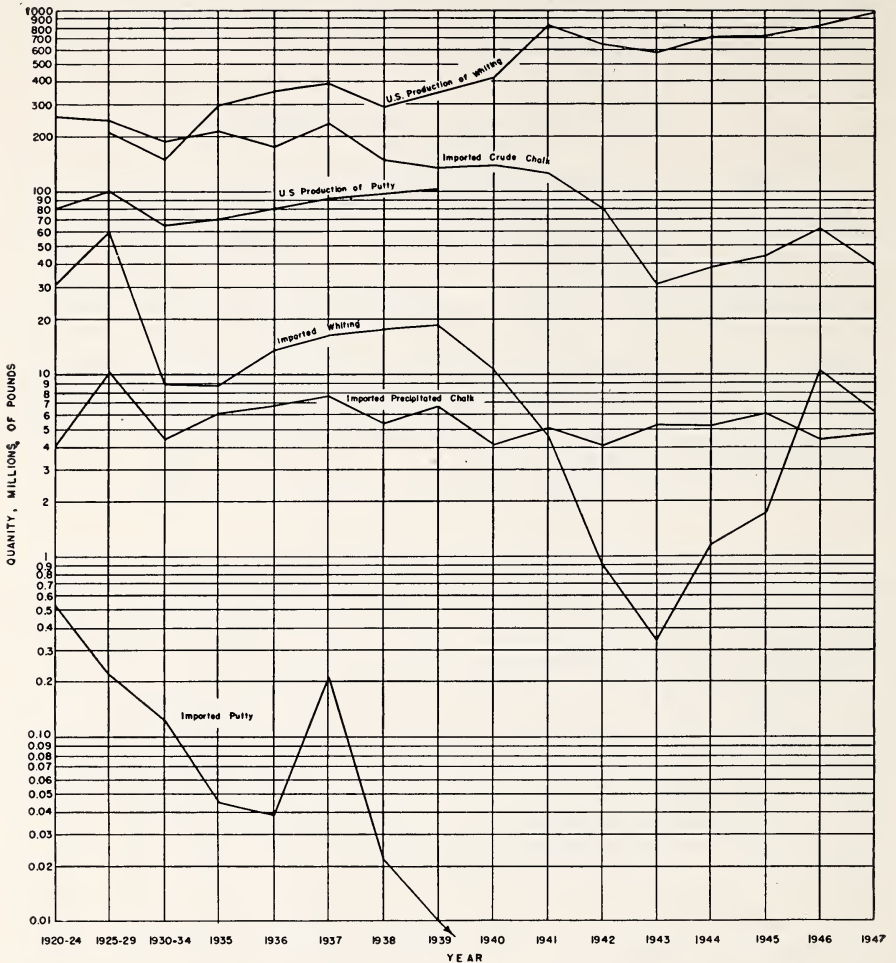


FIG 1—IMPORTS AND PRODUCTION OF CHALK AND WHITING, UNITED STATES, 1920–1948.

Domestic production figures from the U. S. Bureau of Mines; import figures from the Foreign Commerce and Navigation of the United States, U. S. Bureau of Foreign and Domestic Commerce.

The purest natural white calcium carbonate products can be made by grinding the white marbles of Georgia, Vermont, Alabama, California, and other states. Their plasticity is low. Limestones and marbles as sources of calcium carbonate for whiting products can be delivered at a lower cost to the large eastern markets than the domestic chalks of the central and southern states. Therefore the manufacturers of whiting throughout the northeastern United States have adapted them to their service by improved and superior methods of grinding and preparation.

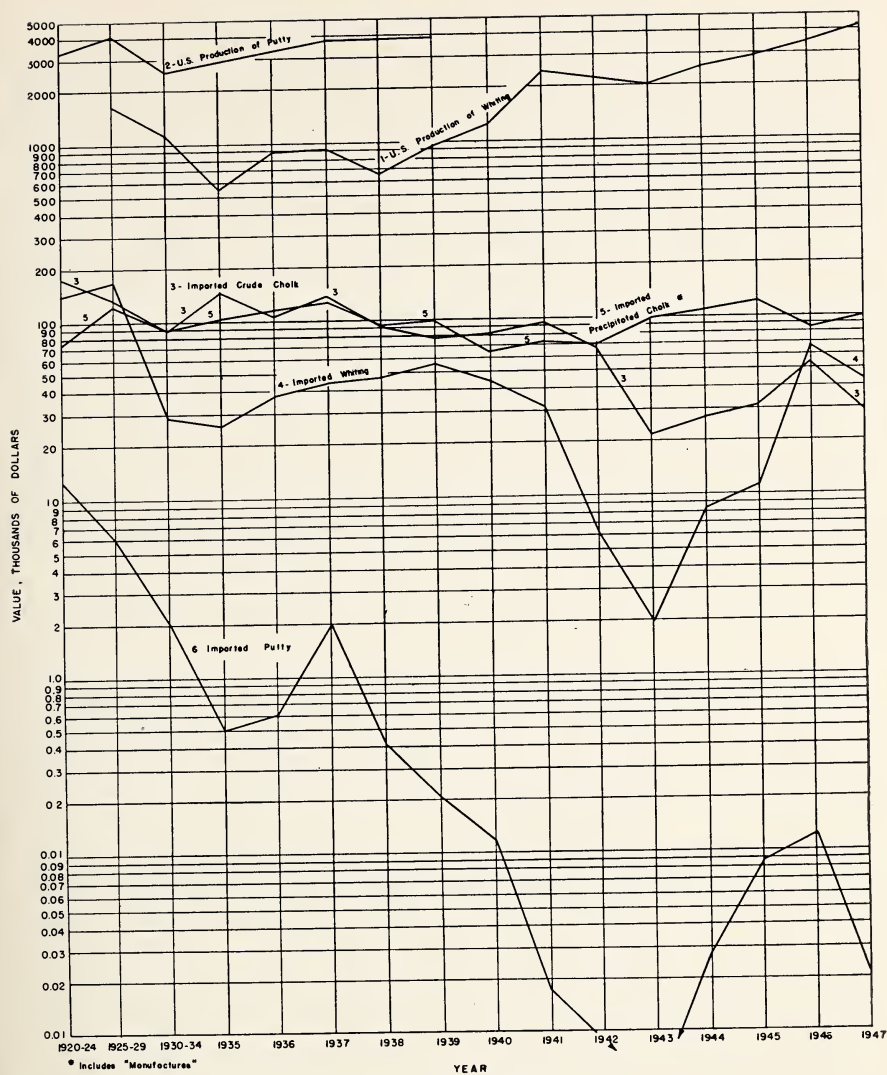


FIG 1 (CONTINUED).

According to the Bureau of Customs, Treasury Department, the tariff rate for 1947, applied to imported whiting or Paris white, dry-ground or bolted, is 0.2¢ per pound; whiting ground in oil (putty) is dutiable at the rate of 0.5¢ per pound; imported precipitated chalk is dutiable at the rate of 15 pct ad valorem and manufactured shapes at the rate of 25 pct ad valorem under Tariff Act of 1930, as modified by several trade agreements. Imported chalk, crude, not ground, bolted, precipitated or otherwise manufactured, is admitted free of duty.

PRODUCTION AND CONSUMPTION

Fig 1 shows the annual quantities and values of imported whiting and products for the period 1920 through 1947 in comparison with the total domestic production of whiting and putty. The domestic production, including ground and precipitated whiting, has shown a healthy growth in this period. European products, largely from England, dropped to a low level during the war, with the exception of water-ground and settled or "precipitated" chalk, which maintained a nearly normal level. The importation, totaling about 15,000 tons of crude chalk in 1943, was less than 5 pct of the American production but undoubtedly was included in the domestic figures for production of whiting. No records have been published for the postwar period.

In 1945, eighteen states produced 49 pct of the 343,220 short tons of ground-limestone whiting, in order of importance as follows: Ohio, Nebraska, Vermont, Tennessee, Illinois, Alabama, New York, Pennsylvania, California, Indiana, Massachusetts, Michigan, Maryland, Oregon, New Jersey, Connecticut, Wisconsin, and Missouri.^{3c}

PROSPECTING, EXPLORATION, MINING, AND PREPARATION

The identification of hard limestone rock is one of the simplest tests in the field because of its moderate hardness of 3 and rapid effervescence with weak acids. However, the hardness test of calcite is inadequate in dealing with the softer chalks and marls, and many impurities minimize the value of the effervescence test. Hence the amount and character of the impurities must be determined by chemical analysis and petrographic studies. Core or churn drilling, prospect adits, or shafts are necessary to determine the extent and uniformity of the deposits unless these properties are indicated by satisfactory exposures. Freedom from grit is an important property in whiting, therefore quartz and other hard impurities must be determined. The removal of a stained overburden in advance of quarrying is very important in securing a white limestone for whiting. Limestone is obtained by both quarrying and mining.

The chapter on Lime and that on Cement Materials, this volume, give the details of occurrence and mining. Chalk, being softer, is mined according to the practice of clays, which likewise vary in hardness from soft muds to flintlike hardness. As very little chalk is mined in this country, the costs for quarrying or mining clay could be used for chalk production, with few exceptions.

Ground Whiting

Chalk whiting made by the older English method is water-ground in edge-runner or stone-drag mills after the flint pebbles have been removed by hand. The milky suspension is classified by settlement in

water in a series of tanks, producing waste sand and coarse particles in the first tank, "commercial," "gilders," "extra gilders," and "Paris white" in the following settling basins. Dewatering is accomplished by siphoning the clear water from the "precipitated" chalk sludge, filter-pressing and drying. The dried product is pulverized, sieved, and packed.

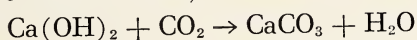
Modern American equipment for wet-ground whiting includes the use of rolls and pebble mills for grinding; bowl and cone classifiers and hydroseparators for classification; and thickeners, continuous filters, and rotary, car or tray driers for dewatering.

In the cheaper dry process, the crushed rock is dried, if necessary, in a rotary drier, coarse-ground in rolls or swing-hammer mills, and finely ground in impact pulverizers, roller mills, ball mills, or air-swept tube mills, often in closed circuit with mechanical pneumatic separators, which produce a product satisfactory for many purposes for which whiting is used. Quartz-lined or porcelain-lined mills and flint pebbles are necessary for grinding the low-iron ceramic whiting. Micronizers, in which attrition takes place between particles rotating at high velocity in a stream of steam or air, have been used successfully for the very fine grinding of whiting.²

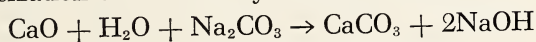
Precipitated Whiting

Three principal methods are used for the chemical precipitation of calcium carbonate, as follows:

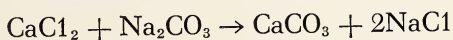
1. Carbonation of milk of lime,



2. Causticization of lime slurry with soda ash,



3. Metathesis of calcium chloride and soda ash,



In the first method, quicklime, obtained by calcining limestone, is slaked, diluted with sufficient water to settle the impurities and then treated with scrubbed carbon dioxide gas, usually produced by burning coke. The precipitated carbonate is dewatered by settling and filter-pressing and the dried filter cakes are pulverized for packing. Very thorough washing is necessary to remove the calcium hydroxide. By method 2, the carbonate is obtained as a by-product in the manufacture of caustic soda in paper mills. Some difficulty has arisen in trying to remove all traces of the caustic soda by washing and holding the pH close to the neutral point for certain requirements, including coating pigments for the best paper.

The third and more recent method²² uses two by-products: (1) calcium chloride from an ammonia-recovery operation:



(2) soda ash, obtained from an ammonia-soda operation in the same factory. Weighed portions of the two solutions are brought together in the reaction tank, the precipitate is thickened and the carbonate slurry is filtered and washed on rotary filters until free of chlorides. The cake, containing about 50 pct water, is pelletized and dried in a tunnel drier, then ground in ball mills.

The original impurities in the limestone, including silicates, manganates, ferrates, aluminates and unburned limestone, have previously been removed from the calcium chloride solution in Dorr settlers.

A special mixing or a ball-milling procedure for the prepared CaCO_3 is required to maintain a low consumption of adhesive in paper-coating mixes corresponding to that of china clay. The improved high-density-kneading method gives a thorough mixing with pastes ranging from 70 to 75 pct solids in dough mixers in the presence of a substantial part of the adhesive.

TESTS AND SPECIFICATIONS

Chemical analysis indicates the purity of whiting, the character of the impurities and something of the color, especially the color that can be expected after ignition; it differentiates between the calcic and dolomitic varieties of limestone. The chemical requirements are particularly important in the chemical and ceramic industries, where a high content of calcium carbonate is required and the impurities, especially iron oxide and manganese compounds, are not wanted.

Alkalinity testing is important for dentifrice, toilet, and chemical products; the curing of rubber is affected by variations in alkalinity, as well as the viscosity of aqueous glaze and body suspensions in ceramics, and saponification of linseed oil in paint and putty can be caused by too great alkalinity. It is to be noted, however, that finely ground pure calcium carbonate, though only slightly soluble in water, can show a pH value greater than 7.8. Both the Federal Government²⁸ and the American Society for Testing Materials²⁷ have titration methods for determining the alkalinity of whittings. Some precipitated whittings are highly alkaline and showed pH values of 8.3 to over 9.6.

The physical properties such as fineness, color, working ability, time of settling, which are essential for most fillers, bear little relation to the chemical composition, comparable enough for factory reliance. Specifications may be based upon the chemical analyses of satisfactory whittings as a preliminary elimination test preceding practical, "proof-of-the-pudding" experiments. With satisfactory properties of the finished product as the ultimate goal, the most direct testing route is introduction of the whiting sample into a commercial batch composition and manufacture of this into the finished product. Small pilot-plant determinations are now common procedures, preceded by elimination

tests for specific chemical and physical properties of the individual constituents. Experienced laboratory technicians can substitute visual color inspection, feel, grit test between the teeth, and other tests for the preliminary tests and proceed directly to the manufacturing test on an experimental basis.

Color often sells the product. Products of black or somber hues can use cheaper whittings of inferior color. For delicate tints, an off-colored cream or gray filler ruins the effect of the pigments, therefore when a variety of delicate colors for paint, rubber, cosmetics or wall coatings are manufactured, it is cheaper and more expedient to standardize upon a few nearly pure white fillers than upon a more complicated stock of white and off-colored raw materials.

Particle-size determinations are made wet or dry with the standard sieves to sizes finer than 325-mesh. For grain less than 50 microns diameter, which represents the bulk of precipitated whittings and many ground products, settling methods, water elutriation, air separators and microscopic examination are used.¹⁷

Following is a brief summary of condensed specifications for the principal products using whiting:

Paint

The refractive index of whiting is too low to make it suitable for use in paint as an opacifier, competing with white lead, the titanates or zinc oxide, but large quantities of whiting are used as extenders and as fillers in oil paints. Whiting has been a principal solid ingredient of the casein and other calcimine coatings from the days of lime white-washed fences.

U. S. Navy Department Specification 52C28 inadequately covers precipitated calcium carbonate whiting as follows: Color, oil absorption, consistency and abrasion tests are compared with a standard sample; "coarse particle (325-mesh) not over 0.5 pct; specific gravity 2.65 to 2.75; composition, CaCO_3 not under 96 pct, MgCO_3 not over 2 pct, SiO_2 not over 0.5 pct, Fe_2O_3 not over 0.05 pct, CaSO_4 not over 1 pct, Al_2O_3 not over 0.30 pct, H_2O not over 0.25 pct."

Very large quantities of domestic whiting, made from ground marbles and limestones, are used in paint. Great improvements have been made in recent years in texture, particle size and degree of whiteness. The chemically precipitated or synthetic whittings at slightly higher costs have better control of the finest particle sizes, give easier grinding and more uniform paint products, are more easily wetted by the vehicle and cause less scouring of the roller mills. It is claimed by some people that the English cliffstone whiting has less activity toward oil than some of the domestic ground materials, which may present a greater tendency to gelation.

Rubber

Specifications for whiting from the rubber industry indicate nearly pure calcium carbonate, which can be supplied by many domestic marbles, limestone, and precipitated whittings.¹⁶ Comparatively little imported whiting is used and apparently has no technical advantage over domestic materials.

Good dispersion due to improved wettability of the filler by rubber is claimed for whiting that has been surface-coated with stearic acid or Tall oil (a mixed fatty and rosin acid recovered from the black liquor of kraft-paper mills).

Various specifications show the following range of requirements from the poorest to the best grades: Color, variable for different products, same as type sample; particle size, 100 pct finer than 100-mesh and 99 to 99.8 pct finer than 325-mesh minimum; ignition loss, 40 to 46 pct minimum; calcium carbonate, 90 to 95 pct minimum; iron, 1.0 to 0.3 pct maximum; manganese, 0.04 to 0.004 pct max; moisture, 0.4 to 0.1 pct max; alkalinity, 1.0 to 0.01 pct max; and physical tests for modulus, tensile strength, and elongation after curing specimens of standard test formulas at different temperatures. Certain precipitated grades for rubber are reported to have a particle size of 0.03 to 0.04 micron.

Linseed-oil Putty

The essential ingredients of linseed-oil putty are whiting and linseed oil. In special cases organic fatty acids, resins or stearates are added for plasticity, stability and wettability. The essential properties are: (1) plasticity, workability, consistency, (2) good adhesion to wood or metal, (3) rapid-hardening ability, (4) low oil absorption, (5) a light gray or cream color, (6) minimum oil separation or "bleeding" on standing, (7) minimum of lumping or setting up in the container on storage, and (8) permanence in service. Plasticity and adhesion vary with the type of whiting particle, the particle size, and distribution of sizes and organic additions. With a given raw material, oil absorption, stability on storage, and workability can be controlled to a large degree by particle size and distribution of sizes. Natural chalks with a natural fine particle size and high specific surface require more oil than ground limestone and marbles. Precipitated whittings require most oil for plasticity.

The traditional use of European cliffstone chalk in putty has been largely superseded by improved methods in preparation of domestic limestones; i.e., finer grinding, blending ground limestone with chemically precipitated whiting, addition of the minimum amount of European chalk, and use of the Mississippi Valley natural chalks. The composition of this low-priced product varies greatly with the freight costs in different parts of the country.

U. S. Navy Department Specification 52W1 (1942) covers a grade of chalk suitable for putty: "Natural chalk by microscopic examination; CaCO_3 not under 95 pct; matter insoluble in HCl not over 3.5 pct; iron and aluminum oxides not over 0.8 pct; putty-making satisfactory in specified formula."

Ceramics^{10,25}

Class 1, ceramic whiting, is limited to a minimum of 96 pct CaCO_3 , a maximum of 1 pct MgCO_3 , 0.25 pct Fe_2O_3 , 2.0 pct SiO_2 and 0.1 pct SO_3 . Class 2 permits 8 pct MgCO_3 . In recent years, the use of iron-free dolomites has been found valuable as a method of introducing MgCO_3 in ceramic bodies and glazes.

USES, MARKETING, AND PRICE

The important uses of chalk and whiting include fillers or extenders in calcimine, oil paints, rubber, putty, paper, oilcloth, linoleum, window shades, cigarette papers, white ink, white shoe dressing, picture-frame moldings, dolls, dyes, tooth paste, fireworks and explosives, wire insulation, caulking compounds, crayons, leather goods, phonograph records, plastics, roofing, tanning, baking powder, animal mineral food, and (coarser grades) in coal-mine dusting.

The disruption of the whiting industries in Europe by the war has given American producers the impetus toward replacement of cliffstone chalk with domestic materials. The extent of the revival of the importation of duty-free crude chalk, with its several physical advantages over ground limestone and marble, is still an unanswered question. A substantial increase is expected because of the comparatively low ocean freight rates for use along the eastern and possibly the western seacoast. The higher rail rates in the middle west are conducive to the continued use of the improved domestic whittings.

The following prices are quoted from the *Oil, Paint and Drug Reporter* (Oct. 18, 1948). They show recent substantial rises in "gilders," surface-treated and precipitated grades.

"Whiting, limestone, dry-ground, 325-mesh, bags, 40 tons, works St. Louis, \$11 per ton, smaller lots \$13.50; wet-ground, air-floated, 325-mesh, 99.5 pct bags, c.l. \$14.50 to \$27.50 per ton; water-floated, extra, "gilders," bags, c.l. \$14.50 to \$28.90 per ton; putty-grade bags, c.l. ton \$13; surface-treated bags, c.l. Ohio, works, \$30 per ton; Paris white, bags, c.l. \$25 to \$31 per ton, l.c.l. \$25 to \$29; precipitated, bags, c.l. \$18 to \$20 per ton, l.c.l. \$22 to \$25."

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CHAPTER 10

CHROMITE*

BY W. D. JOHNSTON, JR.† AND T. P. THAYER†

THE minerals that collectively are known as chromite form an isomorphous series of the general formula $(\text{Mg}, \text{Fe})\text{O} \cdot (\text{Cr}, \text{Al}, \text{Fe})_2\text{O}_3$. So wide is the range in chemical composition in this group that chrome ore consisting entirely of the mineral chromite may range from less than 30 pct to more than 60 pct Cr_2O_3 .

The most comprehensive published data on the chemical composition of chromite are by Stevens,⁶² who made complete analyses of 52 samples of chromite concentrate from many localities in North, Cen-

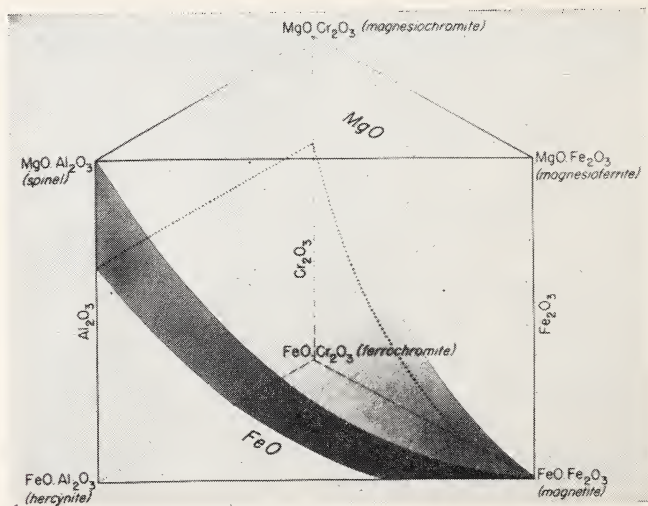


FIG 1—TRIANGULAR PRISM OF COMPOSITION SHOWING END MEMBERS AND PREDOMINANT ZONE OF ISOMORPHISM OF MINERAL CHROMITE (After Stevens).

tral, and South America. These samples were mechanically purified to remove associated silicates and might be regarded as the cleanest chromite that could be obtained by any mechanical milling process.

Fig 1 shows the predominant zone of isomorphism, within the triangular prism of composition defined by the mineralogical end members of the series, wherein his analyzed samples fell.

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† Geologist, U. S. Geological Survey, Washington, D. C.

Fig 2, a triangular diagram of chemical composition divided into fields to which mineralogical names have been given, shows the distribution of Stevens' samples. Most fall within the field that he has named "aluminian chromite." Metallurgical-grade chromite occupies a small part of that field near the $(\text{Mg,Fe})\text{O} \cdot \text{Cr}_2\text{O}_3$ apex of the triangle, and refractory chromite extends down toward the $(\text{Mg,Fe})\text{O} \cdot \text{Al}_2\text{O}_3$ corner in the chromian spinel field.

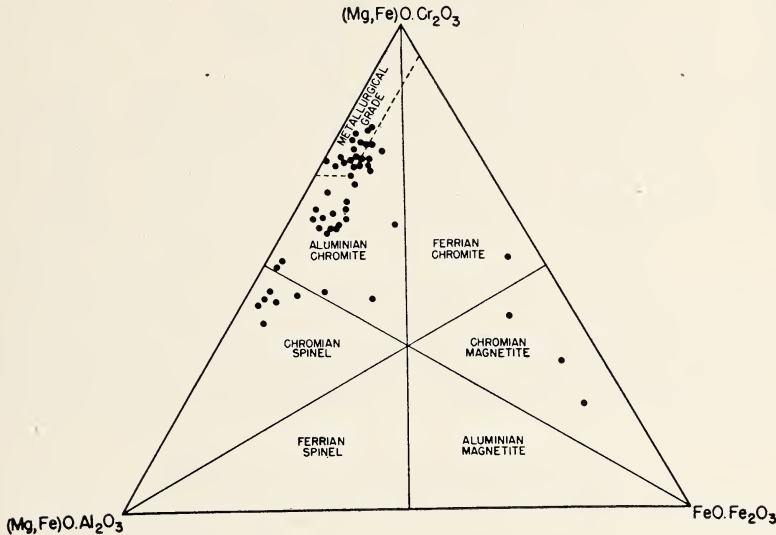


FIG 2—TRIANGULAR DIAGRAM SHOWING COMPOSITION OF CHROMITES AND RELATED MINERALS OF THE SPINEL GROUP IN MOL PER CENT (After Stevens).

Table 1 illustrates the wide range in chemical composition from aluminian chromite containing more than 61 pct Cr_2O_3 to chromian magnetite containing only 13.7 pct.

PROPERTIES

Chromite crystallizes in the isometric system, in octahedrons. Commonly it is massive or fine granular to compact.

The fracture is uneven. It is brittle. Its hardness is about 5.5. Its specific gravity ranges from 4.1 to 4.9. Its luster is submetallic to metallic. It is iron black to brownish black and has a brown streak. In thin section it is translucent to opaque; the high-chrome varieties are red-brown and the high-alumina varieties more coffee brown. Some chromites are feebly magnetic.

The softening point of chrome ore varies from 2300° to 2600°F , depending largely upon the included impurities. Chromite is chemically neutral and almost insoluble in most slags but its reactivity increases and its refractoriness decreases with increase in the amount of iron that it contains.

TABLE 1—*Analyses of Chromite Concentrates*
Rollin E. Stevens, Analyst

Constituent	Composition, Pct ^a							
	1	2	3	4	5	6	7	8
Cr ₂ O ₃	61.10	59.40	56.24	50.99	41.63	43.71	22.31	13.7
Al ₂ O ₃	8.40	10.28	12.42	16.21	25.20	17.34	44.73	3.4
Fe ₂ O ₃	4.31	3.30	4.44	3.44	3.38	7.22	7.04	53.0
FeO.....	10.56	14.09	12.72	14.65	12.29	19.27	7.22	27.4
MgO.....	14.86	12.62	12.47	13.40	16.19	11.00	17.04	1.2
MnO.....	0.15	0.14	0.37	0.23	0.13	0.21	0.16	0.2
CaO.....	0.10	0.14	0.12	0.14	0.16	0.34	0.14	0.3
TiO ₂	0.11	0.14	0.21	0.17	0.30	0.79	0.20	0.5
SiO ₂	0.28	0.12	0.38	0.42	0.36	0.34	0.60	0.3
H ₂ O ⁺	0.04		0.44	0.34	0.24	0.08	0.86	
	99.91	100.24	99.81	99.99	99.88	100.30	100.30	100.00
Cr/Fe ratio.....	3.73	3.07	2.98	2.53	2.40	1.49	1.45	0.16

^a Samples from: (1) Jalapa, Guatemala; (2) Twin Sisters Mountains, Washington; (3) Campo Formosa, Bahia, Brazil; (4) San Luis Obispo, California; (5) Paraguana Peninsula, Venezuela; (6) Stillwater, Montana; (7) Camaguey, Cuba; (8) Casper Mountain, Wyoming.

TYPES OF GEOLOGICAL OCCURRENCE

Chromite is found in ultrabasic rocks or serpentines that have been derived from them. The crystallization of chromite is essentially contemporaneous with the enclosing ultrabasic rocks but some variation in the composition of the chromite itself may result from deuteric reaction with the silicate minerals of the host rock.

Thayer⁶⁶ finds a correlation between the composition of the chromite and the associated rocks. He says: "High-alumina chromites occur in peridotitic masses which contain feldspathic members, and high-chrome chromites occur in feldspar-free peridotites low in alumina and iron. The high-iron chromites of the Bushveld type apparently resulted from crystallization in pyroxenic environments deficient in alumina and relatively rich in iron."

Sampson⁵¹ recognizes the following structural types of chromite occurrences: (1) evenly scattered, (2) schlieren-banded, (3) stratiform, (4) sackform, and (5) fissureform. He says: "The *evenly scattered* class never forms ore, but consists of accessory chromite disseminated through the rock. The *schlieren-banded* class shows bands of concentrated chromite grains, some bands consisting of nearly solid chromite, though more are merely bands enriched in chromite as separated chromite grains. The bands commonly have boundaries which are transitional rather than clear cut. The *stratiform* class is best rep-

resented by the Bushveld, where the chromite forms persistent bands, to which the term strata seems appropriate, in a highly differentiated series. The *sackform* class consists of irregularly rounded ore bodies, commonly of nearly pure chromite grains interlocking. The boundaries of the ore bodies are commonly sharply defined. In the *fissureform* class the introduction of chromite has been controlled by pre-existing fissures."

DISTRIBUTION OF DEPOSITS

United States

Chromite deposits occur in California, Oregon, and Washington as sackform bodies in ultrabasic rocks or in serpentine derived from them. Most deposits are small and exploration and discovery costs are high. Much of the chromite is of metallurgical grade. Characteristic deposits are described in references given in the bibliography at the end of the chapter.

The Stillwater igneous complex outcrops in a belt 30 miles long on the northern edge of the Beartooth Mountains, northeast of Yellowstone Park. The complex is composed of basic rocks and contains more or less continuous stratiform layers of low-grade chromite that yield concentrates averaging less than 40 pct Cr_2O_3 and more than 15 pct Fe. The ore reserve is measured in millions of tons but the grade is so low that it is not normally competitive with foreign ore.

Chromite occurs also in Wyoming, Pennsylvania, Maryland, and North Carolina but these deposits have not produced in recent years. The Wood mine, in Pennsylvania, was the principal world supply in the early days of the chromite industry and contained the largest single body of metallurgical grade that has been found in the United States.

World Deposits

The principal chromite-producing countries of the world are Cuba, Greece, Turkey, Yugoslavia, USSR, Southern Rhodesia, Union of South Africa, India, New Caledonia, and the Philippines. Countries with smaller productions in recent years are Canada, Guatemala, Brazil, Albania, Bulgaria, Cyprus, Iran, Japan, Sierra Leone, and Australia.

Cuba—Cuba has large reserves of refractory-grade ore in the Camaguey district lying near the center of Camaguey Province and smaller reserves in the highly productive Moa district, on the north coast of Oriente Province. The chromite deposits are of the sackform type, occurring like plums in a pudding of serpentinized peridotite. Individual ore bodies range from a few pounds to over 100,000 tons. The Mayari district, in Oriente Province, was the only significant producer of metallurgical ore during World War II. The Cuban deposits are described in detail in references 20, 25, and 64.

Greece—In Macedonia and Thessaly, in the northern part of Greece, chromite occurs in sackform bodies in serpentine. Most of the ore that has been mined is of refractory grade but some ore of metallurgical grade has come from that area. The largest producer before World War II was the Xinia mine, near Domkes, just south of the southern border of Thessaly, which yielded about 2000 metric tons per month in 1943.

Turkey—Chromite is found in many regions in Turkey but the principal production is from the Guleman, Dagardi, and Fethiye districts. It occurs in evenly scattered, schlieren-banded, and sackform bodies in serpentine. Many of the ore bodies have been deformed by postdepositional movements. The grade of ore ranges from 54 to 35 pct Cr_2O_3 . The reserves of all classes of ore are large but exports have been limited mainly to metallurgical ore.

Yugoslavia—The chromite deposits of southeastern Yugoslavia occur in an ultrabasic massif whose gross internal layering suggests a differentiation stratification on a massive scale. The ore bodies are of the evenly scattered, schlieren-banded, and sackform types. Much of the chromite is of metallurgical grade containing 48 pct Cr_2O_3 and a Cr:Fe ratio of 3:1.

USSR—Gubkin's map²³ of 1939 shows 24 chromite localities in Russia, of which two are in the Caucasus, 21 in the Urals and one near Lake Balkhash, eastern Turkistan. The Ural deposits contain chromite of all grades, including metallurgical ore with 50 pct Cr_2O_3 . During World War II a number of shipments of remarkably high-grade metallurgical ore, some of which contained 60 pct Cr_2O_3 with a Cr:Fe ratio of 4:1, were loaded at Murmansk but a description of the deposit from which this ore came has not been found. The largest reserves reported up to 1936 appeared to be of refractory grade, in the central Ural Mountains.

Southern Rhodesia—Most of the chromite production of Southern Rhodesia is from the Selukwe area, where it occurs as schlieren-banded, sackform, and fissureform bodies in a highly altered ultrabasic rock that is locally termed "talc schist." Because of the high chromic oxide content and large reserves, this district is one of the world's most important sources of metallurgical ore.

A second, but genetically dissimilar, district in Southern Rhodesia is the Great Dyke, which extends for 330 miles and has an average width of 4 miles. The Great Dyke is composed of ultrabasic rocks and contains numerous chromite bands or layers of the stratiform type, which, although thin, represent a very large reserve of metallurgical and chemical-grade ores.

Union of South Africa—The Bushveld igneous complex in the

Transvaal probably contains the largest known reserve of chromite in a single geological formation. The chromite occurs in layers from a fraction of an inch to 4 ft thick and ranges from about 35 to 50 pct Cr_2O_3 , with a Cr:Fe ratio of about 1:6. Most of the ore is friable and is well adapted for chemical use, although not desirable for refractory or metallurgical use in the present world market. In 1947, the Transvaal supplied 83 pct of United States imports of chemical ore.

India—During the six years 1934–1939, approximately 266,000 metric tons of chromite was mined in India, of which 48 pct came from Mysore, 36 pct from Baluchistan, and 16 pct from Bihar. In all three districts, the chromite occurs in sackform bodies in serpentine. The Baluchistan chromite is of metallurgical grade and that of Mysore varies greatly from deposit to deposit, ranging from 36 to 50 pct Cr_2O_3 .

New Caledonia—Chromite in New Caledonia occurs as sackform bodies in serpentine and as a residual alluvial blanket upon deeply weathered outcrops of serpentine rocks. The quality of the chrome ore is high; it commonly contains more than 50 pct Cr_2O_3 with a Cr:Fe ratio of more than 3:1. Much New Caledonia ore is friable; hence has been used for the manufacture of chromium chemicals.

The Philippines—The principal Philippine chromite deposits are in the Province of Zambales, on the Island of Luzon. The Masinloc deposit, with a reserve estimated to be of the order of 10 millions of tons, is refractory grade averaging about 33.5 pct Cr_2O_3 and 30 pct Al_2O_3 . Important reserves of metallurgical-grade ore averaging over 50 pct Cr_2O_3 occur in the holdings of the Acoje and Zambales Companies. The Masinloc deposit probably will be the largest producer of refractory ore in the near future.

PRODUCTION AND CONSUMPTION

Fig 3 shows the yearly production of the principal chromite-producing countries from 1880 to 1945. It illustrates both the increasing world consumption of chromite and the principal changes in the chromite supply. World production reached the all-time high in 1943 of 1,973,000 metric tons. Table 2 shows the amount and tenor of ore consumed in the United States.

Domestic chromite production has been important only in time of war. During World War I, a maximum production of 92,322 short tons was attained, in 1918, and during World War II, the domestic production reached 160,120 short tons, in 1943. The latter production, however, includes low-grade chromite from Montana, which normally is not competitive with imported ores.

It is of interest to note that the principal world reserves are of refractory and high-iron chemical grades whereas the present world con-

TABLE 2—*Quantity of Chromite and Tenor of Chromite Ore Used by Primary Consumer Groups in the United States, 1940-1945^a*

Year	Total Chromite Consumed		Tenor of Ore, Percentage of Cr ₂ O ₃		
	Gross Weight, Short Tons	Average Tenor, Percentage of Cr ₂ O ₃	Metallurgical	Refractory	Chemical
1940.....	562,915	45.0	50.5	35.8	47.2
1941.....	800,290	44.3	50.1	34.8	46.3
1942.....	891,952	43.2	48.5	34.0	44.8
1943.....	964,600	43.8	48.5	34.0	44.7
1944.....	848,449	44.1	49.4	34.2	45.7
1945.....	808,120	43.8	49.1	34.2	45.0

^a Minerals Yearbook, 1945.

sumption is mainly of the high-chrome types of ores. This implies the future necessity for a more extensive use of high-iron chromite where such ores can be substituted for high-chrome types.

PROSPECTING AND EXPLORATION

The "sackform" type of deposit, which occurs in apparent random distribution through ultrabasic igneous rocks, is generally found by tracing chromite float to the outcrop. Recent detailed geological work on deposits of this type in California and Oregon has indicated that dunite or serpentine derived from dunite is a more favorable environment than the less basic feldspar-bearing rocks. The gravimeter was used with marked success in the Camaguey district, Cuba, in locating sackform bodies that did not outcrop. Previous geological mapping had restricted the area for gravimeter exploration to the most favorable host rock and topographic conditions were unusually favorable.

The "stratiform" type of deposit, such as occurs in the Stillwater complex in Montana, the Great Dyke in Southern Rhodesia, or the Bushveld complex in South Africa, is followed by tracing outcrops, either directly or by float. Detailed geological study of the complexes has established the petrologic zones to which the chromite layers are confined and so restricted the areas requiring detailed prospecting. As these deposits are essentially tabular, with the same geometry as a sedimentary bed, the variation in width and grade encountered along the strike may safely be considered to be indicative of the width and grade that will be found downdip.

GRADES AND SPECIFICATIONS

The three principal uses of chromite are: (1) metallurgical, (2) refractory, and (3) chemical. Chrome ores or concentrates are generally

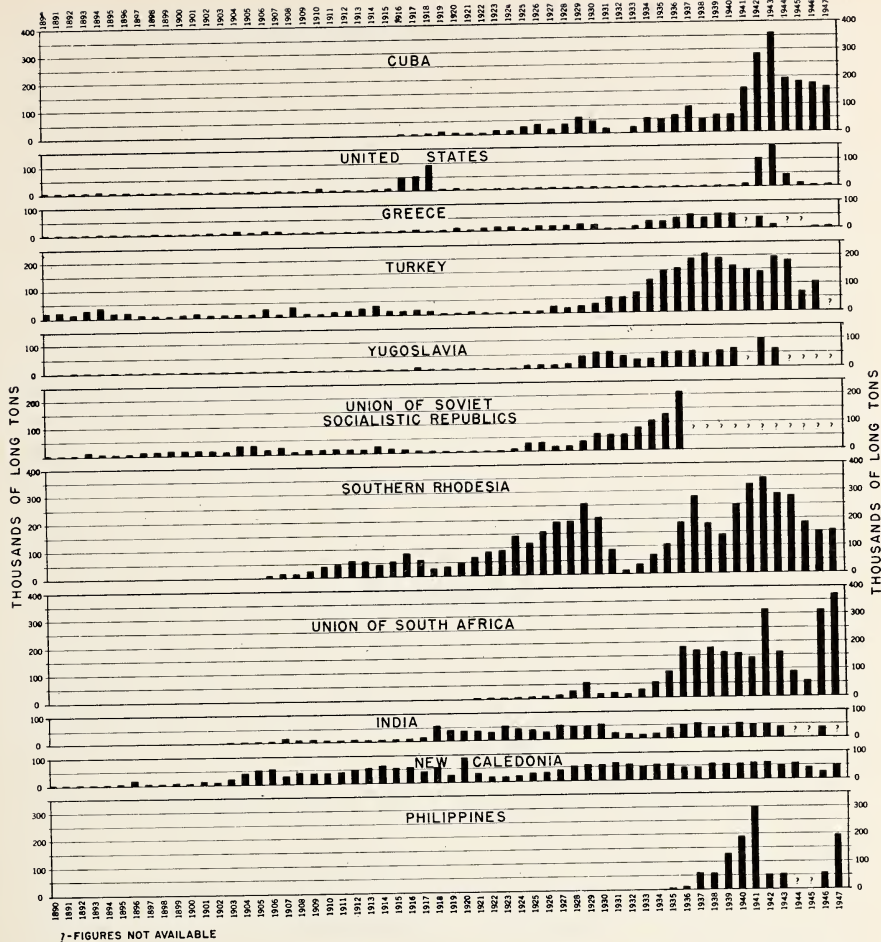


FIG 3—PRODUCTION OF CHROMITE FROM THE PRINCIPAL PRODUCING COUNTRIES.
Data from Mineral Resources of the United States and the Minerals Yearbook.

identified with regard to their suitability for these uses. Typical out-turn analyses of chromite cargoes are given in Table 3.

Specifications for metallurgical chromite normally require a minimum of 48 pct Cr_2O_3 , with a Cr:Fe ratio of 3:1. Penalties and premiums on Cr_2O_3 and the Cr:Fe ratio usually are based on these minima. Generally a hard, lumpy ore is specified but certain metallurgical practices permit the use of soft ore or chromite concentrates. The analyses of the cargoes from Turkey, USSR and Southern Rhodesia, shown in Table 3, are typical of metallurgical-grade chromite.

Refractory ores are high in Cr_2O_3 plus Al_2O_3 and relatively low in Fe and SiO_2 . They are used in making chrome brick, chrome-magnesite brick, plastic cement and other refractory products. The principal limiting factor in the refractoriness of chrome brick is the silicate binding

TABLE 3—*Typical Out-turn Analyses of Chromite Cargoes*

Country	District	Composition, Pct					Cr: Fe Ratio
		Cr ₂ O ₃	Fe	Al ₂ O ₃	MgO	SiO ₂	
Cuba.....	Camaguey	31.03	12.39	27.40	16.99	5.28	1.71
Cuba.....	Oriente (Moa Bay)	36.03	10.93	27.85	17.02	3.31	2.25
Cuba.....	Oriente	44.9	9.9	11.1	19.2	7.6	3.1
United States.....	California	46.14	11.07	11.01	15.42	5.8	2.85
United States.....	Montana	38.80	17.53	15.47	12.42	3.95	1.51
Greece.....		41.83	11.74	11.60		8.98	2.46
Turkey.....		48.76	11.01	12.54	16.80	4.39	3.03
Yugoslavia.....	Serbia	52.59	11.14	9.90	16.79	4.58	3.23
USSR.....		52.47	10.91	9.52	12.36	6.85	3.29
Southern Rhodesia.		49.87	11.50	11.11	15.94	6.39	2.96
Union of So. Africa.	Transvaal	43.97	19.55	15.69	9.99	3.23	1.54
New Caledonia....		46.42	9.83	16.03	17.84	4.56	3.23
Philippines.....	Masinloc	34.22	10.66	30.32	16.47	3.51	2.20
Philippines.....	Florannie	51.72	11.61	11.38	15.93	3.72	3.05

rather than the chrome itself, therefore the amount of silica and fluxes such as lime must be kept to a minimum. In industrial practice, an excess of MgO is added to all chrome ores to combine all the silica in forsterite during firing. The analyses of the cargoes from Camaguey, Cuba, and Masinloc, Philippines, shown in Table 3, are typical of refractory-grade chromite.

Chemical-grade ore should be as high in Cr₂O₃ and as low in SiO₂ and Al₂O₃ as possible. Specifications are more variable than for the other grades and generally are determined for each ore on a basis of price, availability, and past experience. During World War II, the practice was established of regarding as chemical grade ores that were not suited for refractory or metallurgical usage, either because of their chemical composition or their physical characteristics. That practice, however, does not now hold. In Table 3, the soft ore from New Caledonia might be regarded as a high-grade chemical ore whereas the Montana and Union of South Africa ores are somewhat less desirable.

PRICE HISTORY

Refractory and chemical ores sell for about half to two thirds the price of standard metallurgical ores. Since 1930, the base price of 48 pct Cr₂O₃ with a Cr:Fe ratio of 3:1 has ranged from \$18 to \$52.80 per long ton. The operation of the law of supply and demand on chromite prices is shown in Fig 4. Between 1941 and 1945, prices were stabilized by OPA ceilings and Metals Reserve purchases, with refractory ores at \$36.50. Late in 1948, the prices were as follows, per long ton, f.o.b. cars in Atlantic ports:

Percentage of Cr_2O_3	Cr:Fe Ratio	Source	Price
48	3:1	Turkey	\$40-42
48	3:1	{ Rhodesia India }	38-40
50	None specified	Transvaal	29.50
48	None specified	Transvaal	28.50
45	None specified	Transvaal	26.50
44	None specified	Transvaal	20.00
34	Refractory		20-22

Chrome brick were quoted at \$69 per short ton and chrome-magnesite brick at \$80 per short ton, f.o.b. cars at the plant.

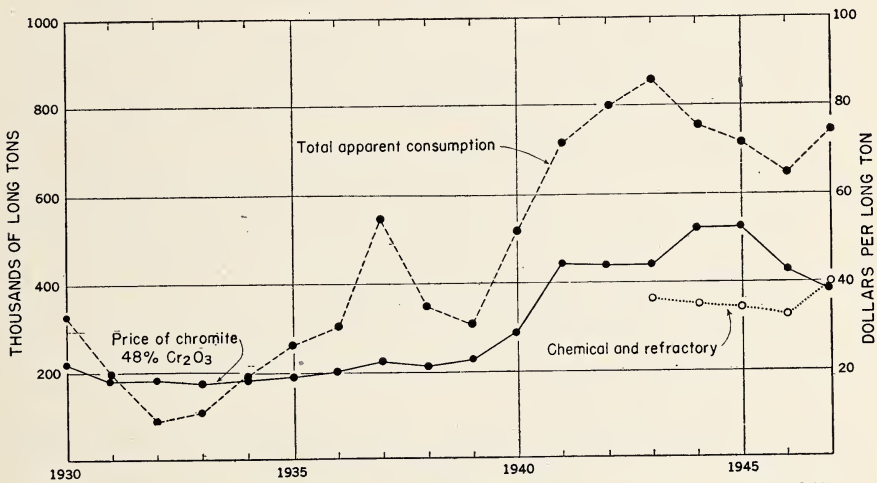


FIG 4—APPARENT DOMESTIC CHROMITE CONSUMPTION AND PRICES, 1930-1947.

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CHAPTER 11

CLAY

By H. RIES*

THE term "clay" is applied usually to certain earthy rocks whose most prominent property is that of plasticity when wet. This permits them to be molded into almost any shape, which they retain when dry. Furthermore, they harden under fire. Clays contain hydrous aluminum silicates—the clay minerals—in appreciable amounts, but aside from this a number of other mineral grains, particularly quartz, may be present. Texturally clays are fine grained, and the so-called true clay particles are usually under 2μ in diameter.

MINERALS IN CLAY

Certain hydrous aluminum silicates that predominate in many clays are known as the clay minerals^{38,82} and are grouped by Kerr⁴¹ as follows:

KAOLIN GROUP	Kaolinite	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
	Dickite	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
	Nacrite	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
	Halloysite	$\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
	Anauxite	$\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
	Allophane	$\text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot n\text{H}_2\text{O}$
MONTMORILLONITE GROUP	Montmorillonite	$(\text{MgCa}) \text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot n\text{H}_2\text{O}$
	Beidellite	$\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$
	Nontronite	$(\text{AlFe})\text{O}_3 \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$
	Saponite	$2\text{MgO} \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$
ALKALI-BEARING CLAY	{ Metabentonite } { Clay mica* }	$\text{K}_2\text{O} \cdot \text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ in variable amounts

* This includes illite.

The kaolin group has been found to consist of a number of minerals with the same chemical composition but different crystalline structures.⁸³

Kaolinite is commonly formed by the weathering of other mineral particles, particularly feldspar, but some deposits, like those in Cornwall, England,³⁶ and others in the Washington-Idaho district, are thought by some to be of hydrothermal origin.

Dickite and nacrite are thought to be due usually to waters of

* Professor of Geology, Emeritus, Cornell University, Ithaca, New York.

hydrothermal origin, the first being formed probably at a lower temperature.^{83,105}

Halloysite is crystalline, as shown by the X-ray, and has a number of lines in common with kaolinite. It may have originated in different ways.⁴¹ It is very fine grained, and may occur as bedlike deposits or crusts. In texture it is powdery, massive or crustified. Two varieties have been recognized, a hydrous form, sometimes termed endellite, and a less hydrated one, the halloysite, which is derived from the former on heating.⁵ It may be associated with kaolinite.⁸⁴

Allophane commonly is glassy and amorphous. Ross and Kerr⁸⁴ consider it to be a solid solution of silica, alumina and water.

Montmorillonite is a common alteration product of glassy particles of volcanic ash in the clays known as bentonites, but it may also have been formed in marine sediments, soils, in gouge clays, and even as a weathering product.^{82,85} Beidellite and nontronite are less common.

Illite, formerly referred to as a sericite-like mineral,^{29,83} is common in sedimentary clays and shales.

Many other minerals have been identified in clays but few of them occur in quantity.⁷³ Those that may be present, sometimes in appreciable amounts, are: quartz, usually in grains of variable size; calcite, usually in fine-grained, perhaps colloidal form, but sometimes as concretions; limonite, often finely distributed as a coating on grains, sometimes as concretions or crusts; gypsum, in grains, selenite plates, crystals or rosettes; siderite, sometimes finely distributed, or occasionally as concretions in some clays and shales; pyrite as grains and concretionary lumps; muscovite, widely distributed, and commonly in very small flakes; rutile, almost universally present but only in scattered grains of microscopic size.

While the clay minerals may form in place from the other minerals in residual or even some sedimentary clays, in some instances undoubtedly they originate under other conditions, as through the combination of colloidal alumina, silica and water. Thus Ross and Kerr describe long grains or worms of kaolinite noted in some Coastal Plain sands, which could not have been transported and did not originate from the quartz grains.⁸² There is also good evidence that kaolinite or other clay minerals may replace quartz as in the indianaites deposits of Indiana^{75,83} and other places.⁸⁴

Identification of Clay Minerals

While the spectrographic microscope has been of great help in studying clay minerals, the perfection of the X-ray method for determining crystal structure has been of tremendous assistance in this work.

Differential thermal analysis is another aid that has been used to

an increasing extent in recent years. By recording the endothermic and exothermic reaction (Fig 1) that take place when the clay is heated to 1000°C , we obtain a characteristic curve for each clay mineral, and even associated minerals.^{22,31,58,97}

Effect of Electrolytes

When thoroughly broken down or dispersed, the particles making up a clay cover a wide range of sizes. Some settle from a dilute suspen-

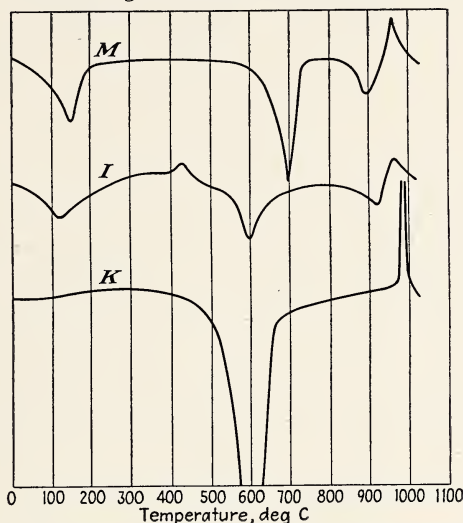


FIG 1—THERMAL CURVES OF TYPICAL CLAY MINERALS.

After Cuthbert.²²

K, kaolinite; I, illite; M, montmorillonite.

sion in a few minutes but others, on account of their very small size, remain in suspension for a long time. These clay particles are negatively charged and may be affected by small amounts of electrolytes, which exert an important influence on their settling properties. Some tend to increase the charge on the clay particles and help to keep them in suspension or dispersed. Such electrolytes are known as dispersing, deflocculating or peptizing agents. Other electrolytes have the opposite effect, in that they tend to reduce the charge on the clay particles, so that they unite, flocculate or coagulate. These may be called coagulating agents, and they reach their maximum effect when the negative charge on the clay particle is reduced to zero.

Clays do not all respond in the same manner to acids or alkalies, because each one may show its own acidity or alkalinity. Furthermore, the presence of soluble salts may exert a modifying effect. Dispersing electrolytes include sodium silicate, sodium hydroxide, sodium carbonate, sodium oxalate, sodium phosphate, and others. Coagulants include acids, sodium chloride, calcium chloride, aluminum chloride,

and so forth. Some electrolytes, like sodium carbonate, may cause deflocculation when added to the clay in small amounts, and coagulation when larger amounts are added.

Base Exchange

The process of base exchange, representing the alteration in cation composition of a solid when treated with a salt solution, is probably of much importance in clays. According to the definition, base exchange may operate with either colloidal particles or larger grains of mineral matter; in other words, it may operate in the weathering of rocks or in fine-grained sediments. Opinions seem to differ as to whether base exchange involves a change in crystal structure. It is probable, however, that it may go on in clays either during or after deposition, and Ross and Kerr⁸⁴ assert that it may take place without any breakdown of the clay molecule as a whole. The former suggests that certain clay minerals and zeolites possess so open a crystal lattice that certain cations can be displaced and other bases substituted in their place without disruption of the primary space lattice. Marshall⁵³ believes that this is the type of base exchange shown by most clays. He has measured the double refraction of clay particles as small as 50 $m\mu$ ($m\mu = 0.00001$ mm) and finds that it varies according to the cation present. Such measurement is possible in clays whose particles show oriented coagulation

TABLE 1—Analyses of Clays

	1	2	3	4	5	6	7	8	9	10	11	12
SiO ₂	46.3	45.78	57.62	59.92	68.62	82.45	54.64	38.07	47.92	49.56	53.12	90.00
Al ₂ O ₃	39.8	36.46	24.00	27.56	14.98	10.92	14.62	9.46	14.40	15.08	18.72	4.60
Fe ₂ O ₃		0.28	1.90	1.03	4.16	1.08	5.69	2.70	3.60	3.44	1.12	1.44
FeO.....		1.08	1.20									
CaO.....		0.50	0.70	tr	1.48	0.22	5.16	15.84	12.30	1.08	1.40	0.10
MgO.....		0.04	0.30	tr	1.09	0.96	2.90	8.50	1.08	7.84	6.92	0.10
K ₂ O.....		} 0.25	{ 0.50 0.20	{ 0.64	3.36	{ }	5.89	2.76	{ 1.20 1.50		5.72 tr	tr tr
Na ₂ O.....												
TiO ₂						1.00			1.22	0.40		0.70
H ₂ O.....	13.9	13.4	10.5	9.7	3.55	2.40	3.74	2.49	4.85	22.96	12.04	} 3.04
Moisture..		2.05	2.7	1.12	2.78		0.85					
CO ₂							4.80	20.46	9.50			
SO ₃			0.35						1.44 ^a			

^a Also 1.34 organic matter.

1. Kaolinite.
2. Washed kaolin, Webster, N. C.
3. Plastic fire clay, St. Louis, Mo.
4. Flint fire clay, Salineville, Ohio
5. Loess, Guthrie Center, Ia.
6. Siliceous clay, Rusk, Tex.
7. Brick shale, Mason City, Ia.

8. Brick clay, Milwaukee, Wis.
9. Shale clay, Ferris, Tex.
10. Bentonite, Otay, Calif.
11. Potash-bearing bentonite, High Bridge, Ky.
12. Sandy brick clay, Colmesneil, Tex.

and works accurately for particles smaller than 500 m μ . He notes also that clays with high base-exchange capacity have a greater capacity for oriented coagulation.

Sodium chloride solution in contact with an ordinary clay results in a displacement of some of the calcium or magnesium in it. Conversely, calcium or magnesium may displace sodium. Only clay minerals with easily replaceable bases, such as calcium, magnesium, potassium or sodium, exhibit much base exchange. The base-exchange capacity is different in different clays. It is highest in montmorillonite, with illite next and kaolinite last.³⁰

Chemical Composition

Clays vary widely in their chemical composition, from those close to kaolinite to others that show a high percentage of impurities (Table 1). A chemical analysis of clay is not usually carried out in detail, so that the TiO₂ is included with the Al₂O₃, instead of being determined separately. All volatile matter is commonly expressed as loss on "ignition." All iron is usually determined as Fe₂O₃. Other unsatisfactory features of the chemical analysis are that it gives little information regarding the physical properties of the clay, or the distribution of the constituents in the samples analyzed.⁷³ Moreover, it is unsafe to attempt to calculate the mineral composition from the bulk analysis. A modification of the ordinary quantitative analysis, known as the "rational analysis," attempts to determine the compounds present. It was first applied to kaolins, which were assumed to consist of quartz, feldspar and kaolinite (clay substance). The method is not reliable, however, and no satisfactory way of making this type of analysis has been devised.⁷³

PROPERTIES OF CLAY

Plasticity

The property of plasticity, already defined, is the outstanding characteristic of clays. They vary from those of high plasticity, or "fat" ones, like the ball clays and bonding clays, to those of low plasticity, termed "lean," and represented by some very sandy ones. The plasticity may be affected by the amount and character of colloidal material, the quantity and proportions of nonplastic particles, the amount of water, as well as salts, bases, acids and organic matter.

The cause of plasticity has been much discussed^{62,73} and has been variously assigned to hydrous aluminum silicates, shape and size of grains, colloidal content, and other attributes. The present general view regarding plasticity is well expressed by Norton, who says: "It is undoubtedly due to an active particle surface, which has the property of attracting to it a stable water film. This attractive force both holds the

water in the pores and the particles together." There is no doubt also that the plasticity is influenced by the thickness and viscosity of the water films around the particles, as well as the size, shape and distribution of the latter.

The plasticity of a clay may be reduced by the addition of non-plastic material. Preheating a clay before use, to temperatures varying from 100° to 300°C, has a similar tendency.¹¹ Greaves-Walker found that the addition of hydrochloric acid to North Carolina shales increased their plasticity.²⁷

While the particle size has sometimes been suggested as the chief cause of plasticity, it has been pointed out by Parmelee that mixtures of very fine-grained clays and coarse-grained ones are more plastic than either of these alone.⁶² Very fine grinding of some minerals gives some plasticity, but nothing like that observed in clays. It is claimed also that an excessively high colloidal content develops stickiness but not plasticity.

Texture

The grains of clay cover a relatively wide range of size, some clays containing sand particles large enough to be recognizable with the naked eye. A large percentage of the particles may be less than 2μ (0.002 mm) in size, and when the clay is thoroughly dispersed the smallest, which are negatively charged, may remain in suspension for days.

In most ceramic work the separation of the particles in a clay is commonly made with sieves, some as small as 300-mesh. Many laboratories use the hydrometer test to determine the sizes from sand down,

TABLE 2—*Mechanical Analyses of Clays Made by Hydrometer^a*

No. ^b	Particles Larger than 2.0 Mm	Coarse Sand, 2.0 to 0.25 Mm	Fine Sand, 0.25 to 0.05 Mm	Silt, 0.05 to 0.005 Mm	Clay Smaller than 0.005 Mm	Colloids Smaller than 0.001 Mm	Passing No. 40 Sieve
1	10	51	25	16	8	6	65
2	3	26	45	16	13	9	85
3	1	14	34	28	24	1	90
4	3	6	23	57	14	0	96
5	0	3	3	6	88	78	97
6	0	1	14	52	33	16	100
7	0	2	9	43	46	22	100
8	0	0	1	14	85	80	100

^a Supplied by U. S. Bureau of Public Roads.

^b 1. Sandy clay from South Carolina. 2. Sandy clay from Madison County, Virginia. 3. Frost-heaving silt soil from New Hampshire. 4. Frost-heaving silt soil from Oregon. 5. Colloidal clay soil productive of landslides in Virginia. 6. Expansive clay from Kansas. 7. Gumbo from Red River Valley, Minnesota. 8. Wyoming bentonite.

and Table 2 gives such a series. By using a supercentrifuge, Marshall⁵³ has separated the smallest particles of clays, as shown in Table 3. These clays, after removal of organic matter, soluble salts and exchangeable bases, were dispersed after bringing to pH9 with NaOH.

TABLE 3—*Mechanical Analyses of Clays by Centrifuge Method*

Clay	Concentration, Pct	2 μ –1 μ	1 μ –0.5 μ	500–200 m μ	200–100 m μ	100–50 m μ	Under 50 m μ
Kaolin.....	0.2	66.0	21.0	7.0	6.0	39.0	
Bentonite ^a	1.0	2.0	31.0	16.0	12.0		
Putnam clay.....	0.5	7.8	6.6	11.8	11.6	21.3	40.9
Rothamsted.....	0.5	15.2	12.1	18.7	14.3	10.3	29.4

^a Approximate values obtained by interpolation in the distribution curve.

Water in Clay

Two kinds of water usually are recognized in clay: (1) mechanically held water, and (2) chemically combined water.

When a clay dries from its plastic condition to a constant weight at room temperature, the water that evaporates until air shrinkage ceases is known as “shrinkage water.” That which is still left in the intergrain spaces is termed “pore water,” and may be driven off at 100°C. The pore water and shrinkage water together are known as the “water of plasticity.” There may also be moisture retained on the surface of the clay particles as a film of molecular dimensions, which is tenaciously held and which is referred to as hygroscopic or micellar water. It may not all pass off until the clay is heated to 200°C. Table 4 gives the range of water of plasticity as recorded for a number of types of clay.⁷³

TABLE 4—*Water of Plasticity of Clays*

Clay	Pct	Clay	Pct
Crude kaolin.....	36.39–44.78	Plastic fire clay.....	13.00–37.00
Washed kaolin.....	44.48–47.50	Flint clay.....	9.00–19.00
White sedimentary kaolin..	28.60–56.25	Brick clay.....	13.00–41.00
Ball clay.....	25.00–53.00	Sewer-pipe clay.....	11.00–36.00
Crucible clay.....	27.00–51.00		

A high percentage of shrinkage water is rather characteristic of fine-grained clays that dry to a strong body and they are likely to show excessive plasticity, high shrinkage, warping and cracking. A high content of pore water characterizes a clay with a porous structure. The ratio of shrinkage water to pore water is said to be important in clays used in the manufacture of crucibles and glass pots⁶² and the best ones

are said to show a ratio of 1:1 between shrinkage water and pore water. Table 5 gives the properties of several clays with respect to water and shrinkage.⁴⁶

TABLE 5—*Water and Shrinkage in Clays*

Clay	Water of Plasticity	Volume Drying Shrinkage	Shrinkage Water	Pore Water	Ratio Pore Water to Shrinkage Water
Kentucky ball.....	54.8	30.3	28.8	26.0	0.90
S. P. G. ball.....	48.2	25.0	21.5	26.7	1.24
English ball.....	40.9	25.8	21.1	19.7	0.93
Georgia kaolin.....	33.5	15.3	11.4	22.0	1.93
Missouri Hercules.....	30.3	18.3	12.7	17.6	1.38

Clay is very hygroscopic and when dry absorbs moisture from the atmosphere, some absorbing as much as 10 pct of its dry weight. The chemically combined water is chiefly that held in combined form as a part of the hydrous aluminum silicates, and passes off mostly at a temperature of 450° to 600°C.

Shrinkage

Clays exhibit two kinds of shrinkage, air and fire. Air shrinkage occurs as the clay dries and continues until the particles are all in contact. It depends in part on the water content and character of the clay, being high in very plastic clays and low in sandy ones. An excessive air shrinkage tends to cause cracking but a low air shrinkage is usually characteristic of clays that dry to a weak and porous body.

Open porous clays are easier to dry than dense, highly plastic ones, for in the latter water evaporates from the surface more rapidly than it can be drawn from the interior, and this develops stresses, which cause cracking. Very plastic clays therefore require slow drying.

Air shrinkage may be recorded in terms of the length or volume of the dry clay, the two being called, respectively, linear and volume shrinkage. Both linear and volume shrinkage may be measured (see Tests, later in the chapter), but the former can also be calculated from the latter.⁷³

Strength

The strength of clay in its dried condition is an important property, as it enables it to withstand shocks in handling of the dried ware; also, a clay of high strength is capable of carrying a larger amount of non-plastic material, without too great deterioration of strength.

Strength of a dried clay may be determined by tension, compression, or transverse tests. The first was formerly much used but is now discarded, the second finds little favor while the third is the one commonly

TABLE 6—*Air Shrinkage of Clays*

Clay	Linear, Pct	Volume, Pct
Crude kaolin.....	5.00- 7.6	14.11-20.92
Washed kaolin.....	3.00-11.0	20.00-29.00
Georgia kaolin.....	4.50-12.5	7.50-36.46
Ball clays.....	5.25-12.0	22.00-32.00
Flint clays.....	0.78- 6.5	2.3 -21.00
Sagger clays.....	3.00-11.0	9.0 -25.00
Paving-brick clays.....	0.90- 6.0	3.5 -18.00
Sewer-pipe clays.....	3.50-10.5	16.12-22.90

employed. It is expressed in terms of the modulus of rupture and is carried out on the clay dried at 110°C, ranging in different clays from a few pounds per square inch to, in extreme cases, over 1000 lb. The figures in Table 7 give some idea of the range of transverse strength in different types of clays.⁷³

TABLE 7—*Range of Transverse Strength in Clays*

Clay	Psi	Clay	Psi
Washed kaolin.....	75- 200	Sewer-pipe clays.....	190- 589
Georgia sedimentary kaolin...	150- 166	Sagger clays.....	46- 474
Ball clays.....	25- 600	Brick clays.....	50-1500
Glass-pot clays.....	173-1068		

The transverse strength of most clays usually decreases when sand or ground flint is added but occasionally it may increase; the clay alone develops minute cracks in drying, which weaken it, but the addition of flint avoids this and the true strength of the clay manifests itself.^{62,73} It has also been shown that the transverse strength of a clay may increase with an increase in its base-exchange capacity.³¹

The bonding strength of a clay refers to its power to hold together particles of nonplastic materials, such as standard sand, potter's flint, or "grog" (crushed brick). The property is important in the use of pottery, glass-pot, and crucible clays,¹² as they have an appreciable amount of nonplastic material mixed with them.

Color

Iron is the commonest coloring agent of raw clays, giving yellow, pink, reds and browns, depending on the amount present and the state of oxidation. Greensand usually gives a green color. Organic matter may color a clay gray or black, sometimes even pink. Clays free from these coloring agents are usually white. Fired clays may owe their color to iron compounds, titanium oxide, or lime reacting with iron, but iron is the usual cause of the color.^{62,73}

The best white-burning clays have less than 1 pct Fe_2O_3 ; those con-

taining 2 pct tend to develop a light cream tint. An exact prediction regarding the color-burning qualities cannot be made from the chemical analysis, partly because it does not show whether the iron is evenly distributed. Buff-burning clays may vary from 1 to 5 pct Fe_2O_3 , but just why this color may be obtained from such a wide iron range is difficult to explain. Most of them have 3 to 4 pct Fe_2O_3 . Red-burning clays have 5 pct or more Fe_2O_3 . Such clays at a low temperature tend to burn pale red or salmon but as the temperature increases they turn to a darker red, and finally to purplish or even greenish purple. The more siliceous clays usually develop a brighter shade of red. Much depends on the kiln atmosphere, for if this is reducing, iron gives a bluish or bluish black color. Some white, cream or buff-burning clays become bluish gray at certain temperatures, owing possibly to the formation of ferrous silicate. This is called bluestoning. Lime in excess of iron oxide, if the two are evenly distributed, gives a cream-colored product, unless overfired, when the clay turns greenish or greenish yellow. Before the iron and lime begin to react, the clay may be pink if enough iron is present. Titanium oxide to the extent of perhaps 2 pct causes a creamy tint. This may explain why some clays very low in iron oxide do not burn white.

Porosity

The porosity of a clay refers to its volume of pore space expressed in terms of its total volume. In raw clay the pores are all open but of variable size. In fired clays the pores may be of variable size, but are of two types, open and closed, the latter being formed by the expansion of gases during fusion. Porosity in the raw clay influences its drying qualities, in that large pores permit the water to escape more rapidly. In fired clays the shape and size of the pores affect the properties of the ware, such as strength, behavior as an absorbent, resistance to weathering, shock, abrasion, corrosion, discoloring agents, efflorescence, destructive action by fungus growths, dielectric strength, and so forth.⁶²

The temperature-porosity relations in firing serve to show the manner and progress of vitrification. Thus a clay in which porosity decreases rapidly, because of sudden fluxing action, is one that vitrifies quickly, and when a rise of the porosity curve quickly follows the drop in porosity it indicates a short firing range, such as would be characteristic of highly calcareous clays.

It is not uncommon to determine the absorption of a fired clay for water, instead of its porosity, since the curve of the former in a general way follows the latter but is always lower.

Specific Gravity

The specific gravity of a clay may be expressed in three different ways:^{62,73}

1. True specific gravity, or the ratio of solid material, exclusive of closed or open pores, to an equal volume of water. This is determined on a powdered sample.

2. Apparent specific gravity, or the ratio of the volume of solids (plus the volume of any closed pores) to an equal volume of water.

3. Bulk specific gravity, or the ratio of the entire volume of material, including solids, closed and open pores, to an equal volume of water.

True specific gravity is affected by the minerals present in the raw clay, and in the fired clay by silica inversion, chemical reactions, fusion and crystallization. The apparent and bulk specific gravity are affected by all of these factors as well as by the porosity. In firing, the true and apparent specific gravity should theoretically decrease, while the bulk specific gravity increases. Change in specific gravity during firing indicates progress of vitrification. Table 8 gives the change in porosity and specific gravity of a Maryland clay.¹¹⁰ Table 9 gives another series of somewhat complete determinations made on Kentucky ball clay.

TABLE 8—*Changes in Specific Gravity and Porosity during Firing*

Temperature, deg C	1150	1200	1250	1275	1300	1325	1350	1375	1400
Porosity, pct.	22.8	22.0	10.1	9.6	6.6	6.3	1.4	0.7	0.4
Volumetric shrinkage, pct.	8.0	8.9	19.1	20.8	17.6	16.1	19.3	19.5	19.5
Apparent specific gravity.....	2.52	2.51	2.42	2.44	2.32	2.29	2.24	2.25	2.25
Bulk specific gravity.....	1.94	1.96	2.18	2.21	2.17	2.14	2.22	2.23	2.24

If the sample tested is a manufactured product, the amount of water and pressure used in molding may influence the results. Therefore there will be a difference in the bulk gravity, depending on whether the ware is slip-cast, hand-molded, plastic, or dry-pressed, if the same material is used.⁴⁶

Firing Changes

When a clay is fired it undergoes various changes in color, hardness, specific gravity, porosity, and other properties. Some of these have already been referred to; others are mentioned in the following paragraphs. These changes may begin at a relatively low temperature range or they may not be completed until higher temperatures are reached.

Loss of Volatile Products

The volatile products liberated during the firing of clay consist of: (1) chemically combined water; (2) organic matter, either carbon or bituminous matter; (3) oxides of sulphur or carbon given off when carbonates, sulphates or sulphides are dissociated. Dehydration of hydrous aluminum silicates takes place chiefly between 450° and 600°C, there being a slight variation in the different ones.^{62,73} Billsite shows from 25 to 30 pct loss at 310°C and diaspore, 12 to 14 pct loss at

TABLE 9—*Determinations on Kentucky Ball Clay^a*

Cone.....	2	6	8	10	12	14
Volume fire shrinkage, pct.....	31.6	34.9	36.7	38.7	39.4	42.2
Apparent porosity, pct.....	21.3	15.8	9.5	2.9	1.1	1.2
Total percentage of pores based on bulk volume of piece.....	22.4	18.4		8.9	6.1	4.1
Closed pores.....	1.3	3.9		6.2	4.0	3.8
Specific gravity:						
Bulk.....	2.09	2.18		2.32	2.39	2.47
True.....	2.69	2.679		2.541	2.515	2.587
Apparent.....	2.65	2.57		2.38	2.41	2.49

^a Made by Parmelee and McVay.

540°C. Hydrous iron oxides generally decompose at 150° to 250°C, although some show the change between 250° and 300°C. Hydrocarbons, which may give trouble in firing, may be completely oxidized and removed by heating at between 800° and 900°C. Calcium carbonate at normal atmospheric pressure decomposes a little below 900°C, although the change may begin earlier. Siderite decomposes at 800°C but in presence of clay this may begin at 425°C.⁶² Pyrite begins to decompose at 350°C while gypsum loses three fourths of its water content between 250° and 400°F and all of its volatile matter by 1100°C.

The two following analyses, representing, (1) an impure clay from Ferris, Texas, and (2) brick from that clay, are interesting as showing the loss of volatile products in firing.⁶⁹

	1	2		1	2
SiO ₂	49.45	56.6	Na ₂ O.....	0.21	1.4
Al ₂ O ₃	17.11	20.4	TiO ₂	0.17	with Al ₂ O ₃
Fe ₂ O ₃	3.45	6.2	H ₂ O.....	4.84	0.5
CaO.....	12.67	11.7	CO ₂	7.10	
MgO.....	1.77	1.4	SO ₂	2.00	
K ₂ O.....	0.13	1.5			
				99.43	99.7

Fusibility

When exposed to a rising temperature, clays do not fuse suddenly; on the contrary, they soften slowly until the entire clay becomes a viscous mass. With impure clays this may occur at a relatively low temperature but with those approaching kaolinite in composition it takes place at a much higher one.

Following dehydration, the clay is porous but after a temperature interval it begins to compact, then the more easily fusible minerals begin to melt, with the formation of glass. With further temperature rise the fluid portion attacks the mineral grains not yet fused, and finally a solution of molten glass is formed.

In the first stages of firing, although the clay may become compacted into a hard mass like common brick, it is said by some that there is no evidence of softening of the particles.⁶² This period has also been called incipient vitrification, but by some that term is used to refer to the stage at which enough glass has been developed to bind the mass together. Complete vitrification would represent the stage reached in the fusion of a clay when sufficient glass has been developed to close all the pores. As the temperature rises and the fluidity of the glass developed increases, the clay mass or object no longer holds its shape, and reaches a condition referred to as viscosity. The temperature at which the development of glass begins, as well as its amount and viscosity, exerts an influence on the behavior of the clay during vitrification. In some clays, glass has been found to develop at a temperature as low as 700°C. The term "vitrification" as applied to clay wares does not always mean the same thing. Paving brick and sewer pipe, for example, are said to be vitrified, but technical difficulties prevent the complete attainment of that condition. Electrical porcelain must approach it very closely.

The stages of incipient vitrification, vitrification and viscosity merge into each other, but the temperature interval between the first point and overfiring is variable. Clays having a long vitrification range are, in general, the safest to use for vitrified wares, as most commercial kilns cannot be controlled within a range of a few degrees of temperature, and there is less danger of the ware becoming overfired and ruined. Clays that begin to overfire as soon as they have reached a condition of vitrification are said to have a short firing range.

The curves of porosity and fire shrinkage shown in Figs 2 and 3 illustrate well the behavior in firing of the two types of clay mentioned above.

Most fire-clay bodies when examined in thin section under the petrographic microscope show a variable amount of glass, depending on the amount of fusion that has taken place during firing, while scattered through this there will be noticed mineral grains that have not yet been affected. Some of these, however, may exhibit a certain amount of corrosion.

Relatively few new minerals will have been found to have crystallized out from the fused material on cooling. Small rods of hematite have been observed in the glassy matrix of some ferruginous clays, but the mineral that has been most often noticed, and which has attracted considerable attention, consists of needlelike grains, usually colorless. For some years these were identified as sillimanite, but later it was discovered that they were the mineral mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). The temperature at which this develops does not seem to be the same always, but it has been observed to form at as low as 900°C. Mullite is

a rare mineral, having been first observed in some igneous rocks on the island of Mull. Commercial deposits are found of the minerals sillimanite, kyanite and andalusite, all of which have the composition Al_2SiO_5 . When these are heated they all change to mullite at temperatures between 1400° and 1550°C . It has been found that the development of mullite in the firing of certain ceramic bodies has great importance, because it imparts to the ware high tensile strength, superior dielectric properties, and low thermal expansion, properties that are particularly valuable in spark plugs. It is possible to use the proper amount of the

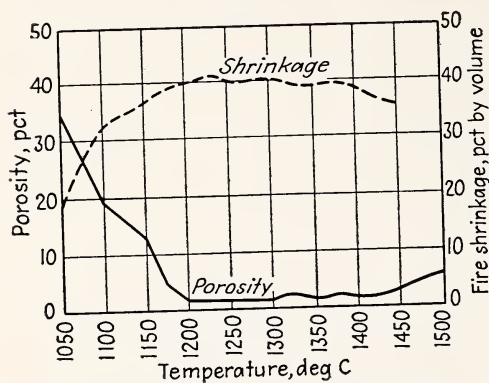


FIG 2—POROSITY AND SHRINKAGE CURVES OF A TENNESSEE BALL CLAY WITH LONG FIRING RANGE. Bleining and Loomis: *Trans. Amer. Ceramic Soc.* (1917) 19.

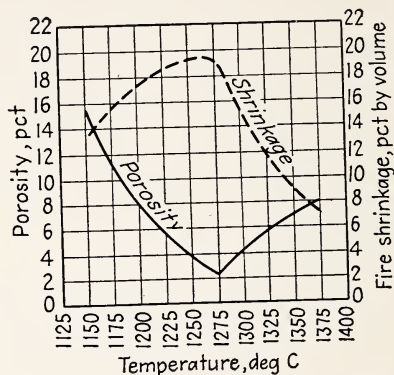


FIG 3—POROSITY AND SHRINKAGE CURVES OF CLAY WITH SHORT FIRING RANGE. Brown: *Jnl. Amer. Ceramic Soc.* (1918) 1.

minerals mentioned in the clay mixture and have them change to mullite in firing.

The fusion point of a clay is usually expressed in terms of Seger cones⁷³ and may range from as low as perhaps cone 1 (1150°C) to cone 35 (1785°C).

Soluble Salts

Many clays contain at least a small percentage of water-soluble inorganic compounds, which are brought to the surface in the drying of the ware, remaining there as a coating, usually white. These soluble salts are mostly sulphates of lime and magnesia but sometimes there are others. Vanadium salts may also cause a stain.⁷¹ Soluble salts may be in the clay when it is taken from the ground or they may form as the result of weathering, as when pyrite is present. They may also be introduced in the water used for mixing the clay. Others may be formed during firing, by the kiln gases carrying oxides of sulphur from the fuel, which, coming in contact with carbonates in the clay in the presence of moisture, convert them into sulphates,^{62,74}

Soluble salts in clays range from zero to 1.5 or 2.0 pct.⁶² They may

be the cause of technical troubles because of: (1) the unsightly coating that they form on some wares, (2) interference with the adherence of a glaze, and (3) disintegration of the product caused by the crystallization of these salts in its pores. Barium compounds sometimes are added to the clay to render the obnoxious salts insoluble.

ORIGIN OF CLAY

Clays may originate from different kinds of rocks, either by the ordinary processes of surface weathering or by the action of solutions, which may be of igneous origin or indirectly of surface origin. In both cases the alternation product is of residual character and the material may be called a residual clay.

The removal of the clays so formed by various agents of erosion and transportation and deposition elsewhere gives rise to a great group of transported clays.

The several ways in which clay deposits originate are brought out by the following classification:⁷³

Classification of Clays

A. Residual clays.

Formed by weathering of rocks *in situ*, or by rising solutions of magmatic or meteoric origin.

I. Kaolins, white and firing white or light cream.

- a. Deposits roughly tabular in form, as when derived from pegmatites, or hydrothermal alteration along fractures.
- b. Blanket deposits from areas of igneous or metamorphic rocks.
- c. Replacement deposits, as Indianinite.
- d. Bedded deposits from feldspathic sandstones.

II. Red-burning residuals, derived from different kinds of rocks.

B. Colluvial clays, practically landslide masses.

C. Transported clays.

I. Deposited in water.

a. Marine clays or shales. Deposits often of great extent.

White-burning clays; ball clays and sedimentary kaolins; refractory clays or shales; buff burning

Impure clays and shales $\left\{ \begin{array}{l} \text{Calcareous.} \\ \text{Noncalcareous.} \end{array} \right.$

b. Lacustrine clays deposited in lakes or swamps.

Fire clays or shales.

Impure clays or shales, red burning.

Calcareous clays, usually surface deposits.

c. Flood-plain clays. Recent ones usually impure and somewhat sandy.

d. Estuarine clays (deposited in estuaries), mostly impure and finely laminated.

e. Delta deposits. Variable purity, often lenticular.

II. Glacial clays found in the drift. Often stony and lacking stratification. May be red or cream burning (calcareous).

III. Wind-formed deposits (some loess).

D. Chemical deposits (doubtful origin).

Residual Clays

Residual clays due to weathering may be formed: (1) by the decomposition of the silicate minerals in rock, the product being a clay; (2) by the solution of a carbonate rock containing clayey impurities, which are left behind as an insoluble residue, and (3) by the disintegration, accompanied occasionally by some solution, of shales.

In case 1, where the decomposition of silicates like feldspar is involved, the clay mineral formed is a hydrous aluminum silicate, such as kaolinite. Residual clays formed by weathering overlie the bedrock formation from which they have been derived. They may grade into it, as is usual when the weathering of silicate rocks is involved, or there may be an abrupt change from clay to bedrock, as in those derived from limestones. While residual clays have formed throughout geologic time, relatively few "fossil" deposits are found, since these clays are easily removed by erosion.

The thickness of such clays is variable; it depends on the depth to which weathering has penetrated the rock and the freedom of the deposit from erosion. Residual clays derived from rocks free or nearly free from iron-bearing minerals are white and represent the true kaolins but most residual clays are stained by oxides of iron.

Laterite is a peculiar type of residual clay, formed under such conditions that silica is largely removed during weathering, leaving alumina and iron hydroxides predominating in the residual mass. Its formation is associated with tropical climates, and a variety of rocks may yield it.¹⁰⁴

Residual clays, usually of ferruginous nature, are found in many parts of the United States, particularly east of the Mississippi and south of the glaciated area. Within the latter they occur only in protected situations.

Residual kaolins are confined mainly to the belt of crystalline rocks of the Atlantic States from Delaware southward, and reach their greatest importance in western North Carolina. Commercially important deposits are also known at one locality in Quebec, and near Spokane, Wash. In England, the largest deposits known are in the Cornwall district, and these have for years been a large contributor to the American pottery industry. Residual clays formed by rising waters are relatively rare, and not as a rule of commercial value. However, such an origin has been ascribed by some to the Cornwall deposits and those of Karlsbad, Czechoslovakia, as well as the Quebec and Washington occurrences.^{36,119}

Transported Clays

Transported clays initially were derived from residual clays, but later on in addition from pre-existing sedimentary deposits. As noted

in the classification, they have been deposited chiefly in water, under a variety of conditions, which affect the extent and also the characters of the deposit. Those of recent geologic age usually are unconsolidated but the older ones, from the Tertiary downward, are often consolidated to shales, although there may be noticeable exceptions, as in some Tertiary and Cretaceous deposits of the United States.

Glacial clays are of limited occurrence and confined to the area of Pleistocene glaciation.

Wind-formed deposits, if this origin is accepted for the loess, are of widespread occurrence in the Great Plains area. Chemical deposits are a debatable group, insofar as workable ones are concerned.

Secondary Changes in Clay Deposits

In areas of crustal disturbance, beds of sedimentary clays and shales are sometimes folded and faulted, and this may result in steeply dipping beds, as along the eastern edge of the Rocky Mountains. Some Paleozoic shale formations of the eastern United States show a regional dip. Weathering often may bring about such changes as leaching of lime carbonate, oxidation of the iron compounds, or opening of the structure. The transportation and redistribution of iron oxide by surface waters may cause the formation of crusts, and sometimes of concretionary masses. Chert concretions are found in residual clays, but most concretions found in sedimentary clays are probably of contemporaneous origin, and may consist of limonite, iron carbonate or lime carbonate.

Shale beds in places are so softened by weathering near the outcrop that they easily yield a plastic mass when ground and mixed with water, but with depth the material may become much harder and occasionally have too little plasticity to be workable.

DISTRIBUTION OF CLAYS AND SHALES

Clays and shales are widely distributed in the United States and Canada, in formations ranging from pre-Cambrian to Recent. The more important types are:

Fire Clays

Under the head of fire clays, we may include all clays that have a fusion point of cone 19⁺ or higher. Certain varieties that are white-firing or nearly so are referred to often under separate names, as kaolin and ball clay. Excluding these, most of the fire clays that are of sedimentary character are used for a variety of purposes.

The ordinary sedimentary fire clays are found in the United States in formations ranging from Carboniferous to Tertiary, exclusive of the Triassic.²⁰ Their geologic distribution in Canada is restricted to Cretaceous and Tertiary.

Foremost among the clays of this group are those found in the Carboniferous of Pennsylvania,⁹¹ Ohio,¹⁰⁰ Kentucky,⁷⁰ Missouri,^{55,107,113} Indiana,¹¹⁴ Illinois,^{44,63} and Maryland.^{66,110} The clays occur at a number of different horizons, and may be associated with coal. Most of the material is plastic fire clay but with it there may be a hard type known as flint clay, which develops little plasticity and which, because of its texture, structure and appearance, has received this special name. It is found particularly in Pennsylvania, Ohio, Maryland, and Kentucky. Many of these fire-clay deposits are worked as open pits but others are reached by drift or shaft. These clays are widely used for firebrick and other refractory wares.

The Lower Cretaceous formations of New Jersey have for years supplied material for the refractory products industry.⁷⁷ They are all plastic clays and are unassociated with coal.

Important deposits of Tertiary refractory clays are worked in western Kentucky and Tennessee.^{61,115} In Texas⁶⁹ and Mississippi,^{51,75} the Tertiary formations supply refractory clays. Those from the latter state have found favor because of their high bonding qualities, of value in the manufacture of glass pots and crucibles. Other Tertiary clays have been developed in California,²³ Washington,¹¹⁷ and Colorado.¹⁹ A unique type of refractory clay is that found in the north central Ozark region of Missouri,⁶ where there is a series of basin-shaped deposits carrying flint clay, and some run rather high in diaspore. These diaspore clays, which Allen thinks have been formed by the alteration of the flint clay by the action of percolating solutions containing CO₂, are of highly refractory character. Clays intermediate in alumina content between flint clay and diaspore are called burly clays in the Missouri district. The No. 1 grade is said to carry 60 to 70 pct alumina.¹¹³

In Canada, fire clays have not been as widely developed, nor are they as widely distributed, as in the United States. The most important deposits are those south of Moosejaw and in southern Saskatchewan. Extensive deposits are known to occur and have been worked around Clayburn, in southwestern British Columbia. A curious series of deposits is known to have been preserved under a heavy cover of glacial drift on the Mattagami and Missinabi Rivers^{21,40} of Ontario. The clays are of Mesozoic age and associated with sand deposits. Although they are reported to be of high quality, their remote location may hinder their commercial development.

Kaolins

In their washed condition, kaolins are used largely in the manufacture of high-grade products, such as white earthenware, porcelain of all kinds as well as fillers for paper and rubber, and other products. They are rather limited in their distribution.

Kaolins resulting from the weathering of pegmatite and granite

are found in the belt of crystalline rocks extending from Delaware to Georgia,⁷⁵ but the only important deposits now worked are those of western North Carolina and to a lesser extent Delaware. The pegmatites of North Carolina may be weathered to a depth of 80 to 100 ft. White residual clays derived from the Oriskany limestone have been worked near Saylorsburg, Pennsylvania, and others formed from schist were mined at South Mountain, Pennsylvania.⁷⁵ Kaolins from weathered dolomite have been mined in southeastern Missouri.⁷⁵ A group of deposits near Spokane, Washington, formed from pegmatite have been used for refractory wares.¹¹⁹

In Canada, the only kaolin deposit that has been worked is near San Remi, Quebec. This is unique in that it is supposed by some to have been formed by the replacement of quartzite, caused by hydrothermal activity.³⁹

The so-called sedimentary kaolins occurring in the Cretaceous of Georgia^{57,94} and South Carolina^{75,112} have been worked for a number of years and have been used in the manufacture of white pottery, refractories, and as a filler. The deposits usually are lens-shaped and may be of considerable extent, as well as thickness. Bauxite is associated with some of them. The product may be purified before shipment to market.

A widely used material is an extensive deposit of white sedimentary clay occurring in the Tertiary (Eocene) of north central Florida.⁸ It has been worked for more than 40 years, and is known to underlie several counties. The material is so exceedingly sandy that it is washed before shipment.^{8,75}

Ball Clays

Ball clays are sedimentary, plastic, refractory clays, which fire white or nearly so. They are used chiefly as one of the ingredients of whiteware and for other purposes where a refractory clay of good bonding power is required.⁹⁶ The chief domestic supply comes from the Tertiary formations of western Kentucky⁷⁰ and western Tennessee,^{41,75,115} where the material occurs as large lenses associated with other refractory clays used for such purposes as firebrick, saggers, bond for abrasives. These different grades may form separate layers at times in the same deposit.⁷⁵ A relatively small amount of ball clay is obtained also from the Cretaceous beds of New Jersey.⁷⁷ The only locality in Canada where ball clay is said to occur is in southern Saskatchewan, and this is remote from important markets.⁵⁴

Stoneware Clays

Clays employed for the better grades of stoneware⁸⁸ are often at least of semirefractory nature and of dense-burning quality.⁶⁹ It is not necessary that they should fire white. Such clays are found in part

associated with the Carboniferous fire clays of the Central States, as well as in the Tertiary and Cretaceous formations of the East, South and West.

Paving-brick and Sewer-pipe Clays and Shales.

As a rule shales rather than clays are employed for paving brick and sewer pipes. There is a large production from the Carboniferous shale formations of the Central States. Some of the Tertiary clays of Texas, California, and Washington have also been used for this purpose. Georgia, Alabama and Mississippi clays and shales have also been used for sewer pipe. Some Carboniferous shale of Nova Scotia has been used for sewer pipe, and the clays of southwestern British Columbia have been similarly employed.

Brick and Tile Clays

Almost all the states have clays or shales that can be used in the manufacture of common brick.^{8-10,16,17,23,27,32,33,46,65-70,76,95,113,117} The materials commonly used are red-burning surface clays of transported or residual types, and the clay sometimes selected is not of the best, especially if it is very sandy, as it makes a porous and weak brick. Probably the largest brickmaking district in the United States is that of the Hudson River Valley. Cream-burning calcareous clays are sometimes employed, not so much from choice as because they happen to be the common type of material in areas where such bricks are made, as around Milwaukee, Wisconsin,⁶⁸ and some parts of Michigan.¹⁷ Shales of Paleozoic age have been used to some extent in the Eastern and Central States.

Bentonite

Bentonite is a sedimentary clay in which the mineral montmorillonite is an important constituent. It has high plasticity and bonding power. It is widely used as a bonding agent in synthetic foundry sands, in drilling muds, and for other purposes. Bentonite is a widely distributed material, and important deposits of it are found in Wyoming,³⁴ South Dakota,⁸⁶ Mississippi, Arizona and Texas. It is also worked in western Canada, and deposits are known in a number of other countries. This clay is treated more in detail in Chapters 5 and 6.

Canada and Europe

In Canada,^{39,40,76} somewhat the same types of clay are used as in the United States. The surface clays are mostly red burning, but around Winnipeg, Manitoba, cream-burning clays are common,⁷⁶ therefore are selected. Silurian shales are used at Toronto and Cretaceous shales in parts of Saskatchewan.

The most important clays of Europe¹⁷ are the kaolin deposits. Those

at Cornwall, England, which have been worked for years and to depths of several hundred feet are widely used,⁸⁶ not only at home but abroad. They are the largest deposits of their type that have been developed anywhere. Also important are the kaolins of Karlsbad, Czechoslovakia, and those worked at several localities in Germany.⁹⁸ The English ball clays are well known to potters, and, like the Cornwall kaolins, have been exported to the United States in quantity. Belgium, Germany and England^{24,106} all contain excellent deposits of fire clay. That from Gross Almerode, Germany, has been exported to the United States for glass-pot manufacture.

POLITICAL AND COMMERCIAL CONTROL, PRODUCTION AND CONSUMPTION

It can hardly be said that control is much of a problem in the clay industry, because the United States is relatively independent of other countries for its supplies of raw clays. Only certain special kinds of high-grade clays have been imported and these have been gradually replaced by domestic materials, except perhaps the highest grade of paper-coating clays.¹⁰⁸

For many years there has been a somewhat steady importation of English kaolin or china clay for use in the manufacture of china, paper, paint, etc. The strong hold this product has had on the American market for years has been due in part probably to its more uniform character. Before the war more than two thirds of the china clay consumed in the United States was imported from England, and as late as 1925, according to Bureau of Mines statistics, the imports were more than the domestic production. The replacement of foreign clays in the pottery and paper industry continued during the depression, and in 1934 the china-clay imports formed less than 20 pct of the domestic consumption. This increase in the use of domestic materials has been due in part to their more careful preparation for the market.

In former years, much English ball clay was imported, the potters in this country preferring it to the American material, which did not vitrify at quite as low a temperature; indeed, when the American ball clays were first developed some of the potters used to the English product were loath to class the domestic product as ball clay. In recent years, however, the domestic clay has replaced the imported ball clays and glass-pot clays.

Since the large majority of the clay-working plants in the United States obtain their supply of raw material from their own deposits, the production of this clay is not listed separately. According to Tyler, roughly 35 million tons of clay was produced in the United States in 1929, but its chief use was in the manufacture of heavy clay products.

Table 10 shows the production of clay that is sold to factories or

firms on a royalty or tonnage basis as reported by the U. S. Bureau of Mines. It consists mostly of high-grade clay used in the manufacture of whiteware, refractories, or for filler in paper, paint, rubber, or fabrics, and in some years is said not to have represented more than 10 pct of all the clay mined. The figures of production do not include clay used in manufacture of portland cement. They do include bentonite, which is used in part for bleaching as well as a variety of other purposes, but not by itself for the manufacture of clay products. Even the fire clay reported does not include all of that type, as many manufacturers of refractories operate their own deposits.

It is interesting to note the rank of the five leading states for production of several types of clay, as shown in Table 11.

Table 12 shows the salient statistics of the clay industry in the United States for 1944 and 1945 as given in Minerals Yearbook of

TABLE 10—*Clay Sold by Producers in the United States^a*

Year	Kaolin or China Clay and Paper Clay, Short Tons	Ball Clay, Short Tons	Fire Clay and Stone-Ware Clay, Short Tons	Fuller's Earth, Short Tons	Bentonite, Short Tons	Miscellaneous, Short Tons	Total	
							Short Tons	Value
1940	833,450	140,707	2,765,247	146,568	251,033	710,515	4,847,549	\$19,633,568
1941	1,087,848	198,445	4,167,567	207,446	354,028	1,210,168	7,225,172	27,037,391
1942	946,588	162,293	4,839,332	204,244	374,967	1,019,663	7,547,087	26,662,697
1943	929,437	147,785	4,701,144	247,258	480,202	850,397	7,380,632	27,654,732
1944	873,056	155,667	6,344,383	294,737	546,768	2,080,717	17,296,328	36,855,275
1945	939,988	174,524	6,090,411	296,368	573,995	10,848,686	18,923,975	43,259,228
1946	1,322,303	243,145	7,907,974	298,752	601,428	16,022,012	30,563,946	60,863,308
1947	1,425,106	269,050	9,074,923	329,068	763,889	21,737,437	33,599,473	74,272,487

^a Data supplied by the U. S. Bureau of Mines.

TABLE 11—*Clay-producing States in 1946, Arranged in Order of Rank*

Rank	Total Value	Total Tonnage	Kaolin and Paper Clay	Ball Clay	Fire Clay and Stone-ware Clay	Bentonite	Fuller's Earth	Miscellaneous, Including Slip Clay and Shale
1	Ga.	Ohio	Ga.	Tenn.	Ohio	Wyo.	Texas	Ill.
2	Pa.	Pa.	S. C.	Ky.	Pa.	S. Dak.	Ga.	Calif.
3	Ohio	Ill.	Fla.	N. J.	Mo.	Miss.	Fla.	Pa.
4	Mo.	Mo.	N. C.	Md.	Ky.	Ariz.	Ill.	Ohio
5	Calif.	Ga.	Pa.		Calif.	Texas	Tenn.	Texas

TABLE 12—*Salient Statistics of the Clay Industry in the United States, 1944-1947^a*

SHORT TONS

Use	1944	1945	1946	1947
Pottery and stoneware.....	288,627	320,147	423,829	449,184
Tile, high grade.....	73,552	111,708	158,279	173,242
Saggers, pins, stilts, wads.....	31,186	35,104	45,721	44,892
Architectural terra cotta.....	4,790	4,305	4,961	20,943
Paper.....	577,150	550,637	697,283	776,580
Rubber.....	66,748	117,736	175,344	186,296
Linoleum and oilcloth.....	9,912	18,004	18,044	25,714
Paints.....	18,141	21,825	23,043	23,618
Cement manufacture.....	2,841,711	3,160,397	4,843,040	5,407,783
Refractories.....	5,283,025	4,729,815	5,267,630	5,830,869
Heavy clay products.....	6,978,411	8,534,484	17,398,598	19,123,371
Miscellaneous.....	1,182,125	1,319,813	1,508,271	1,536,981
Grand total.....	17,295,328	18,923,978	30,563,946	33,599,473
Value.....	\$36,855,275	\$43,259,228	\$60,863,308	\$74,272,487

^a Data supplied by U. S. Bureau of Mines.TABLE 13—*Imports of Clay into the United States^a*

Year	Kaolin or China Clay, Short Tons	Common Blue and Gross Almerode, Short Tons	Fuller's Earth, Short Tons	Other Clay, Short Tons	Total	
					Short Tons	Value
1935-39 avg....	122,232	27,808	2,256	16,922	188,818	\$1,608,395
1940.....	105,567	32,141	474	2,267	140,449	1,159,730
1941.....	85,141	26,825	342	154	112,462	1,151,915
1942.....	63,278	19,790	287	160	83,524	862,907
1943.....	55,565	15,509	157	247	71,478	230,213
1944.....	45,890	17,597	308	2,712	66,507	661,129
1945.....	57,497	17,852	336	1,636	77,321	1,069,820
1946.....	89,233	22,683	194	4,249	116,359	1,736,389
1947.....	82,628	25,849	155	3,768	112,400	1,719,163

^a Data supplied by U. S. Bureau of Mines.

U. S. Bureau Mines. If we compare the tonnage for 1945 with the average of 1931 to 1934 as given in the first edition of this book (*Industrial Minerals and Rocks*. AIME 1937) we find that it is about nine times greater.

In the years 1940 to 1947, all of the clays listed in Table 13 have shown an increased production but bentonite and fuller's earth have more than doubled their output.

TABLE 14—*Clays Exported from the United States*^a

Year	Fire Clays, Short Tons	All Other Clays, Short Tons	Total	
			Short Tons	Value
1935-39 avg.	61,247	87,824	149,071	\$1,819,242
1940.	96,501	87,667	184,168	2,071,366
1941.	91,732	116,120	207,852	2,537,763
1942.	118,101	75,000	193,199	2,042,490
1943.	97,362	66,177	163,539	1,807,517
1944.	87,741	93,463	181,204	2,065,037
1945.	94,602	89,838	184,440	2,256,207
1946.	97,941	116,476	214,417	3,139,910
1947.	110,193	156,930	267,123	4,603,189

^a Minerals Yearbook, U. S. Bureau of Mines.*Imports and Exports*

Table 13 shows the quantity and value of clay imported into the United States for 1935 through 1947. The classification adopted is not thoroughly satisfactory but is the one that has been used for a number of years.

There was an appreciable drop during the war years, and it remains to be seen how much of this will be recovered.

The exports of domestic clay are given in Table 14.

PROSPECTING

A knowledge of the geological characteristics of clay deposits is of considerable aid in prospecting for clays and in making a field examination. All natural exposures as well as artificial cuts should be carefully examined, not losing sight of the fact, however, that on slopes or steep surfaces there may be considerable weathering and sliding of the material, which covers up a portion of the material in place.

In unconsolidated deposits, a carpenter's auger attached to a sufficiently strong pipe may be used for boring the deposit. Such an outfit can be used to depths of 40 or 50 ft but the system should be made in short sections, which can be connected by means of coupling. An auger outfit can be used also for horizontal boring. The data obtained from properly located boreholes can be used to determine both vertical and horizontal variations in the deposit.

In recent years, power augers and rotary drills have been widely used, especially for extensive prospecting. They can penetrate to greater depths than hand augers, can make holes with larger diameters, and also reduce the cost of operation.

The samples obtained with power augers are not as free from contamination as those obtained with core drills.

A drive pipe drill with a split core barrel can also be employed. A special core barrel that prevents soft, wet material from running out when the pipe is withdrawn is sometimes employed.

If large samples are desired, test pits can be sunk in the deposit. Clay deposits are sometimes prospected by tunnels and shafts.

Sampling

The Committee on Standards of the American Ceramic Society³ recommends that for preliminary testing the body of clay shall be stripped of loose or foreign materials and a series of straight, parallel trenches cut entirely across the outcrop. If the deposit is stratified and the beds dip, the trenches shall be cut across the dip. Each trench should be 12 in. wide and deep enough to yield 100 lb of material. If natural outcrops are not available, preliminary trials may be made with a hand auger, and test pits can be dug for further sampling. Should the deposit show beds that are visibly different from each other, they should be sampled separately. If preliminary tests show the deposit to be satisfactory, the deposit as a whole can be bored or drilled throughout its extent, spacing the holes not more than 100 ft apart.

The samples collected from the different trenches are to be reduced to lumps not over 2 in. in diameter, mixed together, and reduced by quartering to 100 lb.

Too much stress cannot be laid on the fact that all samples collected should represent the average of the deposit or the bed. Furthermore, the clay should be carefully tested before a plant is erected. The writer has known of several plants erected on sites of improperly tested deposits; the result being failure of the enterprise.

MINING

Most clay deposits are worked as open pits, the method of excavation depending on the character of the clay, thickness and extent of beds, and character of the overburden. Where the deposit is small, or consists of beds of different quality, which it is desirable to separate, the clay may be dug by spades or mattocks. Selective mining of different beds is practiced in New Jersey, western Kentucky and Tennessee, and also in part of California. Linton⁵⁰ states that in some California deposits more than 20 ft thick, beds as thin as 2 ft may be separated in selective mining. With thicker beds, and a working face not more than 20 ft high, a power shovel may be employed.

At some clay pits the face of clay, if not too high, may be undercut at the base while wedges are driven in at the top, thus causing a slice of the bank to fall and break up the clay, so that it can be more readily handled. If the clay deposit has a horizontal surface of some

extent, it may be loosened by plows and the clay then gathered up by wheel or drag scrapers.

Shale banks often are blasted and the material that accumulates at the bottom is gathered up by power shovels. Occasionally shale is worked by a planer, consisting of a steel structure^{47,55} carrying a power-driven steel chain provided with teeth, which scrape off pieces of shale. These pieces fall to the base of the face and from there are carried by an endless belt to hoppers or vehicles. Such planers can cut a vertical or steeply sloping face. Depending on their construction, they can work on a straight line or cut a circular swath through an angle of 180°. A similar machine provided with small buckets has been used in soft clay.

For removal of overburden, the methods used may be similar to those employed for excavating clay. In some places drag scrapers on cables are employed, or if the overburden is sandy or gravelly it can be removed by hydraulicking. At one shale bank near Seattle, Washington, where the stripping was 50 to 75 ft thick, this method was used. The sale of the sand and gravel for concrete and other work paid for the cost of stripping. The amount of overburden that can be stripped economically depends on the thickness of the clay and its market value. Linton⁵⁰ describing clay mining in California, says that the ratio of overburden thickness to that of clay varies from 1:1.2 to 1:1.75. In Tennessee as much as 35 ft of overburden has been removed to dig 10 ft of ball clay.

In North Carolina, where the Kaolin mines were in narrow pegmatite dikes, the material was worked by circular pits 15 to 25 ft in diameter, lined with cribbing. As the more recently worked deposits are of greater extent, the kaolin usually is worked with a power shovel, although at one time hydraulicking was used. The latter method has been used also in Cornwall, England, where the pits may be 200 ft deep or more.

In Florida, the clays have been excavated with a clamshell dredge floating in the pit. The material is dumped onto barges or pumped ashore through large pipes to the washing plant.

Underground mining is often used for extracting the higher grades of bedded clay, and usually is carried out by the room-and-pillar method. It has been extensively used in some of the fire-clay deposits of the central and Appalachian states, as well as in parts of California.

In Colorado, along the foothills, where the clay beds dip steeply, and may be interbedded with sandstones, the beds are worked down the dip and along the strike, leaving pillars of hard clay to support the walls. Timbers also may be used to support the hanging wall.

The clay is hauled by different methods from the bank or mine to the shipping bins or manufacturing plant. At pits close to the plant,

auto trucks are commonly used. For longer distances, trains of cars hauled by electricity or steam are preferred. Where the mine entrance is on a mountainside at some distance above the valley, gravity planes or wire-rope trams may be used to bring the clay down to the storage bins or plant.

At one Georgia kaolin deposit, the clay is blunged at the mine and pumped to a washing plant several miles distant.

Relatively few figures giving the cost of mining clays have been published, although Tyler gave a number collected from different sources some years ago.¹⁰⁸

PREPARATION, TESTS AND SPECIFICATIONS

Preparation

Clays used for the commoner grades of clay products, and even for firebrick, do not undergo much preparation, except the removal of pieces of stone. Even ball clays are not put through any purification before shipment.

Kaolins, whether residual or sedimentary, because of their sandy character when mined, are commonly purified to remove the sand, and in some cases also the mica.

Formerly, in brief, the clay was disintegrated in a log washer, the sand then separated, and the water with suspended clay passed along troughs to separate fine sand, after which the clay-water mixture was run into settling troughs.

At present the clay may be refined by a process involving grinding, washing, screening, tabling and classification, and settling. Sodium silicate is added in the early stages to deflocculate the clay, and in the final settling tanks alum is added to the suspension to flocculate the clay particles and cause more rapid settling. The small mica scales are also separated in the process and form a by-product.¹⁰²

Air separation is used sometimes and is finding greater favor.¹⁰⁸ Centrifuges also are used to remove fine grit and to separate the finest particles where the product is sold for coating clay. The iron is removed by continuous ferrofilters.

Weathering may improve the plasticity, and soluble salts may be brought to the surface and washed away; on the other hand, new ones may form, such as ferrous sulphate from pyrite in the clay.

Other forms of preparation are carried out at the factory after the clay has entered the manufacturing process, and need not be considered here.

Tests

Tests of clay are made primarily to measure their physical properties, and certain tests have been recommended by the Committee on

Standards of the American Ceramic Society,³ which apply to clay to be used in its fired condition.

PLASTICITY, FINENESS, AND WATER OF PLASTICITY

There is no standard test for determining the plasticity of a clay, although several different ones have been suggested.^{62,73} It is often determined by feel.

The fineness of clay may be tested by washing the sample through sieves and determining the weight remaining on each. Sieves are not fine enough to separate the smaller particles of clay, and for this purpose the hydrometer method,¹⁵ as used successfully by the U. S. Bureau of Public Roads, can be employed. Similar results are obtainable by the pipette method. The ordinary elutriator is not to be recommended, even though it has been much used in Europe.

Water of plasticity is determined by weighing the freshly molded test piece, air-drying, then again weighing after oven-drying at 110°C. The difference in weight is water of plasticity, which is calculated in percentage of the dry weight.

SHRINKAGE

The drying volume shrinkage is determined by placing a molded test piece in kerosene in a volumeter, of which there are several kinds.^{62,73} After drying, the piece is soaked in kerosene for 12 hr, then placed in the volumeter to determine its dry volume. The percentage of shrinkage can then be determined in terms of the dry volume.

The linear shrinkage can be calculated from the percentage of volume shrinkage by the formula:

$$\text{Linear shrinkage} = \left[1 - \sqrt[3]{1 - \frac{b}{100}} \right] \times 100$$

in which b equals percentage of volume shrinkage. The linear shrinkage can also be determined by making a line of known length on the freshly molded test piece and measuring again when dried.

For shrinkage determinations of the fired pieces, the same methods are employed using water instead of kerosene in the volumeter.

Shrinkage and Pore Water—The data obtained in determining volume shrinkage are employed here. Thus, for shrinkage water:

$$t_1 = \frac{V_p - V_d}{W_d} \times 100$$

in which t_1 = percentage of shrinkage water,

V_p = plastic volume, cc,

V_d = dry volume, cc,

W_d = dry (100°C) weight, grams.

Pore water is obtained from the formula

$$t_2 = T - t_1$$

in which t_2 = percentage pore water,
 T = percentage of water of plasticity,
 t_1 = percentage shrinkage water.

SLAKING AND TRANSVERSE STRENGTH

Slaking Test—A 1-in. cube, consisting of a mixture of 500 pct clay ground to pass a 30-mesh sieve and 50 pct potter's flint, is cut from a slab of the plastic material. This is dried in room temperature, then at 64° to 76°C, and finally at 110°C. It is cooled in a dessicator and then immersed in water on a 2½-in. sieve. The time for it to disintegrate completely is noted.

Transverse Strength—The plastic clay is molded into bars 7 in. long and 1 in. square. These are first carefully dried at room temperature, then at 64° to 76° and then at 110°C. They are cooled in a dessicator and broken in a machine in which they rest on supports 5 in. apart, the load being applied at the rate of about 100 lb per minute. The modulus of rupture is calculated by the formula

$$MR = \frac{3Wl}{2bh^2}$$

when MR = modulus of rupture, psi,
 W = breaking load, lb,
 l = distance between knife-edges, in.,
 b = breadth of bar, in.,
 h = height of bar, in.

Since the clay shrinks in drying, the breadth and height of the bar must be measured before testing. Ten bars should be broken, and vary by not more than 15 pct from the average.

FIRING TESTS

Test pieces are fired over a range of temperature that depends on the type of clay, at a rate of 45°C per hour up to a little below the point of drawing trials, and after that at a rate of 20°C per hour. The fired trials are examined for color, hardness, shrinkage, porosity, and other properties. The fusibility is determined by grinding the clay to pass a No. 60 sieve, molding it into tetrahedra 30 mm high and 7 mm on a side at the base, and testing these in comparison with standard cones of similar size in a furnace with neutral or oxidizing atmosphere.

SPECIFIC GRAVITY

The true specific gravity is determined in the usual manner in a pycnometer. The apparent specific gravity of a fired clay is determined by the formula

$$Ga = \frac{Wf \rightarrow}{Vf - (Sf - Wf)}$$

and the bulk specific gravity by

$$Gb = \frac{Wf}{Vf}$$

in which Wf = weight of fired piece, grams,

Vf = volume of fired piece, cc,

Sf = weight of saturated fired piece, grams.

ABSORPTION AND APPARENT POROSITY

For fired pieces absorption is determined by weighing the dry piece, soaking in water for 24 hr, then weighing again. The increase in weight is calculated in percentage terms of the dry weight.

Apparent porosity is calculated by means of the following formula:

$$\frac{Sf - Wf}{Vf} \times 100$$

Saturation is obtained by soaking the test piece in distilled water at 20°C for 100 hr and boiling for 1 hr during the first, twenty-fifth, forty-ninth and seventy-third hours.

Specifications

While no standard specifications have been recommended, it is always possible for the consumer to prepare them himself, indicating what properties the raw material shall possess.

MARKETING AND USES

Marketing

Clays may be sold under some name or number or under the name of the use to which they are put. This might mean that one clay might be sold under two different names.

Producers of the cheaper types of clay products, such as building brick, drain tile and even common red earthenware, with hardly any exceptions, obtain their clay from their own deposits. Only the kaolins, slip clays, paper clays, many refractory clays, bentonite and fuller's earth (see chapters on bentonite and bleaching clay), as a rule, are mined by separate companies or individuals, and sold to consumers by the ton.

Some clays and shales are sold on a royalty basis, this being quoted¹⁰⁸ as 5¢ a ton for common clays and shales, 10¢ for moderate-duty fire clay, and 10 to 25¢ for high-grade fire clay. The white-burning clays bring the highest prices on the market but for any one type of

clay the price may vary, depending on the amount of preparation it goes through before being shipped.

Refractory clays are rarely shipped long distances to market, unless by water, but china clays and paper clays, because of their more restricted distribution, will stand a longer haul. The two great white-ware potting centers of the United States are Trenton, New Jersey, and East Liverpool, Ohio, but the nearest important domestic sources of white clay are western North Carolina, the Georgia-South Carolina belt, and Florida. The chief markets for these clays are in the central and northeastern states, and this means an appreciable freight rate.

China clay from South Carolina and Georgia,* No. 1, air-floated bulk, sold for \$8 to \$9 per ton and North Carolina ceramic grade was \$18 to \$22 early in 1949.

According to the Bureau of Mines, domestic ball clay sold for \$3 to \$18.25, depending on the quality and degree of preparation. Fire clays averaged \$2.52. Sagger clays sold for as little as \$2.50 but the processed types sold for \$6 to \$25, or even higher. Bentonite crude in 1945 brought \$2 to \$13 per ton but prepared ranged from \$7.50 to \$16.

Uses

Clays may be used in their unfired or fired condition. The properties that govern the use of clays in their raw condition are color, texture, bonding strength and absorptive qualities. The uses to which unfired clays are put include:

Paper clays, usually kaolins of residual or sedimentary character. Whiteness, fineness and uniformity of texture are of prime importance. Somewhat similar clays are used as fillers in fabrics and in manufacture of ultramarine. This group may be designated as "fillers." The requisite properties of fillers as specified by different consumers, either as groups or individuals, are somewhat conflicting, but whiteness and freedom from grit seem to be the essentials.¹¹¹

Bentonite, aside from its use as a bleaching agent, is used as a drilling mud in petroleum industry and as a bonding agent in synthetic foundry sands, which represent two important uses. It is also employed for stopping leakage in soils, dams and rock fractures underground, as well as in the manufacture of plastics.

Fire clays are employed in their raw condition as a bond for synthetic foundry sands.

Common clays may be used for making stabilized roads, in which is employed a properly proportioned mixture of gravel or crushed stone, sand and clay. The clay should be tested for its cohesiveness, which commonly is done by the Atterberg test.⁷³

In its fired condition, clay may be used for a variety of purposes,

* Engineering and Mining Journal (1949) 150, 85.

prominent among which are structural, refractory, decorative and household. The deciding factor is the physical behavior of the clay in both its raw and its fired condition. While different types of clay may be designated by certain names, such as china, brick, stoneware, terra cotta, such terms refer only in a general way to their properties and do not indicate restricted uses. Thus a clay suitable for brick might also be used for drain tile, or a paving-brick clay could also be used for sewer pipes. Furthermore, many clay products other than the cheapest are often made of a mixture of clays, in order to get a material with suitable properties. Architectural terra cotta and chemical stoneware are made usually from a mixture of clays. Whiteware contains kaolin, ball clay, ground quartz and ground feldspar. Any reference to the uses of clay, therefore, might better be expressed in terms of physical properties than in terms of names. The following classification, given by Parmelee,⁶³ brings out these points:

CERAMIC USE CLASSIFICATION OF CLAYS

I. Clay burning white or cream, not calcareous.

A. Open-burning clays (i.e., still distinctly porous) at cone 15 (2606°F).

Uses: If of good color or of good strength, is used for pottery. If of good or high degree of refractoriness, used for various refractories; if also of good color, used for special refractories (e.g., pots for melting optical glass).

1. Low strength. Type: residual kaolins of North Carolina.
2. Medium and high strength. Type: secondary kaolins of Florida and Georgia.

B. Dense burning (i.e., becoming nearly or completely nonporous) between cones 10 and 15 (2426° and 2606°F). Medium to high strength, medium shrinkage.

a. Nonrefractory clays.

3. Good color. Uses: pottery, including certain whiteware, porcelains, stoneware.
4. Poor color. Uses: stoneware, terra cotta, abrasive wheels, zinc retorts, face brick, saggars.

b. Refractory clays.

5. Good color. Uses: refractories, especially for glass if they do not overburn seriously for five cones (about 1800°F) higher. Also uses stated in 3.

C. Dense burning between cones 5 and 10 (2246° to 2426°F) and do not overburn seriously at five cones (about 1800°F) higher than the temperature at which minimum porosity is reached.

a. Nonrefractory clays, medium to high strength, medium shrinkage.

6. Good color; usually reach minimum porosity between cones 5 and 8 (2246° to 2354°F). Type: ball clays. Uses: pottery, whiteware, porcelain and stoneware.
7. Poor color. Uses: stoneware, terra cotta, abrasive wheels, zinc retorts, face brick, saggars.

b. Refractory clays.

8. Dense burning at cone 5 (2246°F); do not seriously overburn for 12 cones (about 432°F) higher; highly refractory; softening point at cone

31 (3182°F) or higher; bonding strength minimum, 325 psi. Use: graphite crucibles for melting brass.

9. Dense burning at cone 8 (2354°F); not overfiring at cones 13 or 14 (2550°F). Strength and softening point as in 8.
Use: steel crucibles.

10. Dense burning at cone 8 (2354°F); not overfiring at cone 15 (2606°F). Bonding strength, 250 psi or higher. Softening point, cone 29 or higher.
Use: glass pots.

II. Buff-burning clay.

A. Refractory clays.

- a. Open burning (5 pct porosity or more) at cone 15 (2606°F) or above. Indurated. Nonplastic or slightly plastic (unless weathered). Type: flint clays.
 11. Alumina 40 pct or less. Use: refractories.
 12. High alumina (over 40 pct). Type: diaspore clays. Uses: refractories, abrasives.
- b. Open burning (5 pct porosity or more) at cone 15 (2606°F) but plastic.
 13. Silica 65 pct or less. Uses: firebrick and other refractories, terra cotta, sanitary ware, glazed and enameled brick.
 14. High silica (over 65 pct). Type: many New Jersey fire clays. Uses: firebrick and other refractories.
- c. Dense burning (porosity under 5 pct) between cones 10 and 15 (2426° to 2606°F).
 15. Medium to high strength, not overburning for five cones (about 1800°F) higher than point of minimum porosity. Uses: glass pots, firebrick, saggers, and other refractories; architectural terra cotta, sanitary ware, enameled and face brick.
- d. Dense burning (porosity under 5 pct) at cone 10 (2426°F) or lower.
 16. (See 8.) Uses: zinc retorts, firebrick, saggers and miscellaneous refractories.
 17. (See 9.) Uses: architectural terra cotta, sanitary ware, enameled and face bricks.
 18. (See 10.) face bricks.

B. Nonrefractory clays.

- a. Open burning (5 pct porosity or more) at cones lower than 10 (2426°F).
 19. High or medium strength. Uses: architectural terra cotta, stoneware, yellow ware, face brick, sanitary ware.
 20. Low strength. Use: brick.
- b. Dense burning (porosity under 5 pct) at cones lower than 10 (2426°F).
 21. High or medium strength. Uses: architectural terra cotta, stoneware, abrasive wheels, sanitary ware, face brick, paving brick.

III. Clays burning red, brown, or other dark colors.

- A. Open burning (do not attain low porosity at any temperature short of actual fusion).
 22. Medium or high strength. Uses: brick, drain tile, hollow blocks, flower pots, pencil clays, ballast.
 23. Low strength. Use: brick.
- B. Dense-burning clays.
 - a. Having a long vitrification range (5 cones or about 1800°F).
 24. High or medium strength. Uses: conduits, sewer pipe, paving brick, floor tiles or quarries, electrical porcelain, cooking ware, silo block, art-ware, face brick, architectural terra cotta, roofing tile.
 25. Low strength. Uses: as dust body in manufacture of electrical porcelain, floor tile, building brick.

b. Having a short vitrification range:

26. High or medium strength. Uses: building brick, face brick, hollow block, flower pots.

c. Highly fusible, forming a glass at about cone 5 (2246°F).

27. Slip clays.

IV. Clays burning light gray or light cream.

28. Containing calcium or magnesium carbonate or both. Never attain low porosity. Very short heat range. Use: common brick.

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CHAPTER 12

CRUSHED STONE*

By A. T. GOLDBECK†

THE use of stone as a building material in relatively large blocks is recorded in ancient historical records but only within the past 200 years has broken stone in small sizes begun to have extensive use, principally in highway construction. Tresaguet, in 1764, describing his method for highway construction in France, required the top surface to be built of stone about the size of a walnut, broken by the use of a hammer. It is said that the Romans, in the top layer of their rather massive roads, used large stones bonded together with lime mortar and bedded in small stones mixed with mortar. Much of the early macadam as built by McAdam around 1815 in England was made with hand-sledged broken stone.

In 1858, the use of crushed or broken stone received a great impetus from the invention in that year by Eli Whitney Blake of what is said to be the world's first stone crusher. As a consequence of that invention, stone could be crushed to small sizes with considerable ease and, as a natural result, the use of crushed stone in macadam roads and as railroad ballast increased at a great rate. Also, as portland cement came into use, machine-produced crushed stone furnished readily available aggregate. Rapidly, other uses developed, such as for fluxstone in the production of pig iron and for other metallurgical operations and chemical utilizations. These utilizations made for the rapid growth of the crushed-stone industry and this growth is still proceeding with the growth of population and the development of new uses, notably the employment of limestone for the improvement of soils for agricultural purposes. The industries of which the production of crushed stone is a part have a tonnage second only to that of mineral fuel in the mineral industries of this country.

* Grateful acknowledgment is made of the generous cooperation and assistance of Bror Nordberg, Editor of *Rock Products*, in giving the benefit of his observations and supplying references concerning recent developments in operating methods. The author has also used the chapter by Seely B. Patterson in the 1937 edition of *Industrial Minerals and Rocks* (pp. 795-836) as a basis for the present chapter. Much of the material in Mr. Patterson's article required no revision to make it currently applicable, but wherever necessary for that purpose, revisions have been made.

† Engineering Director, National Crushed Stone Association, Washington, D. C.

In this chapter will be discussed the production and use of commercial crushed stone, metallurgical stone and other products of the stone industry not treated elsewhere in this volume.

SOURCES AND CLASSIFICATION

Crushed stone is produced from all three groups of rocks on the earth's surface—igneous, sedimentary, and metamorphic. It has been estimated that the lithosphere, the solid portion of the earth's crust, is composed of: igneous rocks, 95 pct; shale, 4 pct; sandstone, 0.75 pct; limestone, 0.25 pct. However, these percentages by no means represent the percentages of crushed stone produced of the several types of rock. The igneous rocks have solidified from a molten state, either at the earth's surface or at various depths; sedimentary rocks have been formed either through the consolidation of the products of former rock disintegration—for illustration, sandstone,—or they have been formed from an accumulation of organic remains, chiefly of a calcareous nature, as typified by limestone and dolomite; metamorphic rocks have been produced by the action of physical and chemical forces such as heat, pressure and moisture on both the sedimentary and the igneous rocks. Thus, gneisses and schists are the metamorphosed form of granite, while marble has resulted from the alteration of sedimentary rocks such as limestone.

Economic availability and commercial usefulness control the quantities of the respective rock types produced, so notwithstanding the relatively small percentage of limestone available on the earth's surface, limestone has by far the greatest production of any of the rocks. The igneous rocks found in southern New England, New York, New Jersey, and Pennsylvania are relatively small outcrops, but they furnish a large tonnage of the production of this type of material, which is found also in the Appalachian and the Pacific Coast states.

The terms "trap rock" and "granite" as used in the crushed-stone industry include various rock types, trap rock generally including all dense, dark, fine-grained igneous rocks such as basalt, diabase or andesite, while granite includes the coarser-grained igneous rocks, particularly those of lighter color such as true granite and syenite. In general, trap rocks are the hardest and toughest of the rocks commercially produced and are valued greatly for their use as railroad ballast and road metal. As a rule, the granites, probably because of their coarse crystalline structure, are not as tough as the fine-grained igneous rocks.

The sedimentary rocks are of greatest importance to the crushed-stone industry, for, as already stated, it is from these rocks that the greatest tonnage is produced. They vary widely in their characteristics, depending on their composition and on the physical forces to which they have been subjected during their formation.

Among the limestones is found material so soft that it is considered unsuitable for structural purposes, but because of its purity it finds great usefulness in the chemical, metallurgical and agricultural industries. Limestones, as a rule, are not as hard and tough as the igneous rocks but they are widely used and highly regarded as structural materials in concrete and in the various forms of highway construction. Because of their nonabrasive characteristic as well as their lesser hardness and toughness, they are much more economical to produce than the more resistant types of rock.

Sandstone is used commercially for various structural purposes. Different deposits differ widely in their characteristics. Certain sandstones are so soft that they can be crushed readily into sand, which is used as a fine aggregate, while other fine-grained sandstones possess a hardness and toughness equivalent to that of trap rock.

Among the metamorphic rocks, quartzite and marble are of the greatest importance to industry. Marble furnishes a large tonnage for practically all the purposes of construction and it furnishes an important source of raw material for burning lime. Quartzite is used as a source of silica in the manufacture of refractories and glass.

Certain porous forms of volcanic rocks—pumice, volcanic scoria, and tuff—are used for various purposes to a minor extent; for instance, as subballast and ballast for railroads and light-weight aggregate for insulation of buildings.

Classification of Rocks

The following classification of rocks is given from the standpoint of the engineer rather than that of the geologist. Most of the rocks in Table 1 are used in one form or another in various types of construction. This classification has been used for many years, particularly by the road builder and the structural engineer. It was proposed originally by Dr. E. C. E. Lord in United States Department of Agriculture *Bulletin* 31, entitled Examination and Classification of Rocks for Road Building.

The igneous rocks are divided into two types, the intrusive, or deep-seated rocks, and the extrusive, or volcanic types. The intrusive rocks in general are the coarse crystalline types and their mineral constituents are well defined; for instance, the granites. Members of the extrusive or volcanic types solidified more rapidly at the surface and are either fine-grained, glassy, or vesicular or have a porphyritic structure, characterized by large crystals in a more or less dense, fine-grained groundmass. As to be expected, the characteristics of these extreme types merge into one another.

Igneous rocks vary in color from white, gray, pink, and brown of the acid granites, syenites and their volcanic equivalents, rhyolite, andesite,

TABLE 1—*General Classification of Rocks*

CLASS	TYPE	FAMILY
I. Igneous	1. Intrusive (plutonic)	a. Granite
		b. Syenite
		c. Diorite
		d. Gabbro
		e. Peridotite
	2. Extrusive (volcanic)	a. Rhyolite
		b. Trachyte
		c. Andesite
		d. Basalt and diabase
II. Sedimentary	1. Calcareous	a. Limestone
		b. Dolomite
	2. Siliceous	a. Shale
		b. Sandstone
III. Metamorphic	1. Foliated	c. Chert (flint)
		a. Gneiss
		b. Schist
	2. Nonfoliated	c. Amphibolite
		a. Slate
		b. Quartzite
		c. Eclogite
		d. Marble

and others, to dark, steel gray or black of the basic gabbro, peridotite, diabase and basalt. These fine-grained igneous rocks are generally dark in color and commonly are called traps, derived from the Swedish word *trappa*, for stair. Rocks of this type frequently break into large tabular masses resembling steps. A typical example is the diabase on the west shore of the Hudson River extending north to Haverstraw. Granites and traps are exceedingly important in the structural field.

The sedimentary rocks are the consolidated products of former rocks that have disintegrated—for instance, sandstone, conglomerate, shale—or they may have been formed by the consolidation of organic remains as limestone and dolomite. Frequently these fragmental materials have been deposited by water, thereby producing a characteristic stratified structure. Some of the sedimentary types—for instance, opal, flint, chert—have been formed by chemical precipitation. Some of the limestones, the oölitic type, are formed of small grains of calcium carbonate cemented together by a calcareous cement.

Unconsolidated products of former rock types may form sands, gravels, silts, and clays. This unconsolidated material may pass through the process of induration into consolidated masses; clay may become shale; shale in turn may become slate. Sandstones resulting from the

consolidation of sand and the cementation of the sand grains are either calcareous, ferruginous, argillaceous, or siliceous, depending on their cementing materials. They form an important class of rocks, used in the past very largely as building stone. Such material is given common names by the trade, such as flagstone, brownstone, bluestone, graystone.

Rocks of the metamorphic class result from the prolonged action of physical and chemical forces such as heat, pressure or moisture, acting on both sedimentary and igneous rocks. The foliated type, characterized by the gneisses and schists, have a peculiar foliated or banded structure, as the name implies, due to the parallel arrangement of their minerals. Nonfoliated types include the marbles and quartzites and have resulted from the alteration of sedimentary rocks without materially affecting the structure and chemical composition of the original material. The metamorphic rocks vary greatly in color, pure marbles and quartzites being white or gray while the gneisses, schists, amphibolites, and others are dark gray to green. These green varieties are known commonly as greenstone or greenstone schist.

Mineral Composition of Rocks

No doubt the mineral composition as well as the structure of rocks plays an important part in controlling their suitability for different structural work and it is the combination of these important factors that makes certain rocks especially useful for particular purposes. Trap rock is highly regarded for uses in which high resistance to impact and loads is important, as in railroad ballast, and at the same time resistance to the disintegrating action of the weather. The high calcium carbonate content of limestones makes them particularly important for chemical and metallurgical purposes and for the treatment of soil for agricultural purposes.

Certain mineral constituents in rocks are detrimental, especially when these rocks are used as aggregates in concrete. For illustration, minerals like beidellite, which expand considerably upon exposure to the weather, make for unsoundness when they occur in certain types of limestone. Marcasite, a form of iron sulphide, may produce detrimental effects in concrete due to expansion upon oxidation and even iron pyrites may produce rust stains on the surface of concrete and thus become an undesirable constituent when present in large quantities. On the other hand, many limestones contain iron sulphide in such minute quantities that no harm seems to result. Opaline silica is typical of certain minerals that are detrimental in concrete, especially when used with cement having a relatively high alkali content, as it is claimed that excessive internal expansion of the concrete may take place through the formation of sodium silicate.

Undoubtedly, the chemical composition and structure of the rocks

TABLE 2—Average Mineral Composition of Rocks (Principal Minerals Only)

Rock	Mineral Composition, Pct													
	Quartz	Orthoclase	Plagioclase	Augite	Hornblende	Calcite	Dolomite	Chlorite	Biotite	Muscovite	Epidote	Magnetite	Rock Glass	Microcline
1. Granite.....	31.0	45.8	7.3						3.8	3.4				3.7
2. Biotite-granite.....	28.0	36.1	12.2						10.5					4.4
3. Hornblende-granite.....	24.9	40.8	9.7		14.7				4.7					
4. Augite-syenite....		60.1	4.7	7.8										9.9
5. Diorite.....	6.2	5.6	33.0		34.0									
6. Augite-diorite....		22.0	29.6	14.8	13.3				4.5			5.2		
7. Gabbro.....			42.7	26.3	11.0									
8. Peridotite.....				16.0								30.6		
9. Rhyolite.....	38.0	42.1												20.0
10. Andesite.....	9.7		45.7	8.6										
11. Fresh basalt.....			36.1	45.0										
12. Altered basalt....			28.6	24.9										
13. Fresh diabase....			48.8	44.4										
14. Altered diabase..			37.4	20.2										
15. Limestone.....						82.3								
16. Dolomite.....							78.6							
17. Sandstone.....	71.2													
18. Feldspathic sandstone.....	42.1	24.3												
19. Calcareous sandstone.....	39.6	17.3				35.3								
20. Chert.....	94.2													
21. Granite-gneiss....	37.2	41.1							4.7	4.9				
22. Hornblende-gneiss.....	11.1	18.4			53.4									
23. Biotite-gneiss....	40.9	33.2							12.9					
24. Mica schist.....	39.3	14.8							14.6	19.2				
25. Biotite schist....	27.3	13.7							38.7					
26. Chlorite schist....	19.9	10.1						36.3			20.4			
27. Hornblende schist	11.3		6.9		62.5									
28. Amphibolite.....			6.5		71.0						10.7			
29. Slate.....		25.9								63.8				
30. Quartzite.....	86.2													
31. Feldspathic-quartzite.....	46.3	33.7												
32. Pyroxene-quartzite.....	36.0		25.1	22.2										
33. Eclogite.....			28.8	14.5										
34. Epidosite.....	16.8				13.6						64.9			

play an important part in their behavior and for important structures—for instance, large dams—it is usual to make a thorough mineralogical as well as a physical investigation of the properties of the rock proposed for use. Table 2 is intended to give merely a rough idea of the average composition of the different rock varieties. Only the principal minerals are listed; those that occur in greatest abundance.

Physical Properties

The physical properties of crushed stone are very important not only in the production of the stone but also in its use. Frequently they

must be considered in choosing the production machinery, for certain types of crushing equipment cannot be used economically when the rock is extremely abrasive. Also, the hardness and toughness of the rock will control certain quarrying practices, such as drilling and blasting. Consequently, the cost of production is greatly influenced by the physical properties of the rock.

The service behavior of rock depends to a very considerable extent upon the properties that control its strength, such as hardness and toughness. Cleavage plays a part in blasting practices and also in the shape of the finished product. The color, as a rule, is not of any great importance except for special purposes, as for use in roofing in the field of decorative floor finishes, and for colored mortar or concrete facings. To obtain beautiful effects with colored aggregates, the surface mortar is cleaned away before it has attained a hard set.

The basic physical properties of aggregates that affect their behavior when used for various structural purposes are hardness, toughness, and the properties that control the resistance of the rock to the disrupting action of weathering agents. Absorption may be important, especially when considered in combination with other physical properties of the rock. High absorption, however, is not necessarily detrimental. Certain fundamental tests for the physical properties of rock have been made for many years and although they are now being displaced by other tests they are still important and are being used in some localities. The hardness of rock for road building is measured by the Dorry hardness test, which measures the resistance of the rock to surface abrasion. A core 25 mm in diameter is drilled from the rock and is held against a revolving steel disk upon which crushed quartz sand of 30 to 40-mesh is fed. At the end of 1000 revolutions of the disk, the loss in weight (W) of the core is determined and the coefficient of hardness is equal to $20 - W/3$.

By toughness of rock is meant its resistance to impact. The toughness test is made by means of the Page impact machine, using a cylindrical core 25 mm in diameter and 25 mm in height drilled from the rock specimen. This core is mounted on the flat anvil of the machine and upon it rests a 1-kg plunger having a spherical end of 1-cm radius. A 2-kg hammer falls from successively increasing heights of 1 cm upon the plunger, and finally the core fractures. The height in centimeters through which the hammer falls is taken as the toughness of the rock.

The Deval abrasion test is still used in some laboratories for determining abrasion resistance. It consists of a cast-iron cylinder 20 cm in diameter and 34 cm long, inclined at 30° with the horizontal axis, about which it is rotated at the rate of 30 to 33 rpm. A sample of stone is prepared consisting of 50 pieces, broken to approximately cubical shape and weighing 5 kg. At the end of 10,000 revolutions, the loss in weight is determined by sieving through a U. S. Standard No. 12 sieve and the

percentage of wear is calculated from the loss of weight thus determined. The French coefficient of wear equals 40 divided by the percentage of wear. Modifications of the Deval abrasion test are practiced in some localities by the introduction of a charge of steel shot with the sample of stone. This modified procedure results in a higher percentage of wear than the unmodified test, probably because of the impact action of the steel charge. The Deval test is partly an impact test and partly a hardness test, but it is generally spoken of as an abrasion type of test.

Of late years the Los Angeles abrasion test has replaced the Deval abrasion test, the toughness and the Dorry hardness tests in many localities, and it is said to closely represent service behavior of crushed stone when used as a highway material. The Los Angeles abrasion machine consists essentially of a cylindrical steel drum 28 in. in diameter and 20 in. long mounted so as to rotate about its principal axis. A radial shelf 4 in. wide extends from end to end inside the drum. The sample of rock should be taken from commercially produced material and the gradation of the sample is selected from a number of standard gradations to most nearly represent the sizes of the material being used in service. The details of the test are fully described in the Standards of the American Society for Testing Materials. Generally, a 5000-gram sample of this graded material is used together with a charge of steel shot weighing 5000 grams. The drum is rotated for 500 revolutions at the rate of 30 to 33 rpm and at the end of the test the amount of loss is determined.

The Los Angeles abrasion test is much more severe and gives higher percentages of loss than the Deval test. To some extent the loss depends upon the shape of the particles in the sample. A very flat and angular shape will give a higher percentage of loss than a cubical shape, the materials being the same. This test measures the combined properties of hardness and toughness of the rock and generally it is considered a rather satisfactory quality test for rock for use in highway building. It is applied also to ballast testing although its agreement with the service behavior of railroad ballast is not thoroughly established.

The crushing-strength test is not practiced as a rule except on stone intended for building purposes. The fact is that most rocks have adequate compressive resistance for structural purposes. Crushed stone does not lend itself to the compression test very readily unless the sample is taken from the ledge rock before it is crushed. Generally the specimen consists of a 2-in. core 2 in. high. The ends must be carefully finished to a flat surface and the bearing blocks must be ground to as flat a surface as possible. No capping material should be used on the ends of the specimen during the test. Pressure is expressed in terms of pounds per square inch of ultimate load.

The specific gravity of rock is the term used to express the rela-

tionship between the weight of the rock and the weight of an equal volume of water. The ASTM has recognized different kinds of specific gravity as applied to aggregates, the principal of which are bulk specific gravity and apparent specific gravity. Bulk specific gravity is the ratio of the weight in air of a given volume of a permeable material, including both its permeable and impermeable voids, in relation to the weight of an equal volume of distilled water. The volume of rock in this case is the volume that would be enclosed by an impermeable membrane of zero thickness stretched around the surface of the rock. Apparent specific gravity is the ratio of the weight in air of a given volume of the impermeable portion of a permeable material—that is, the solid rock including its impermeable voids or pores—in relation to the weight in air of the same volume of distilled water. The volume of rock considered in this case is the same as in the case of bulk specific gravity minus the volume of the permeable voids.

The present standard method for determining bulk and apparent specific gravities is the so-called wire-basket method. The sample, weighing about 5 kg, is oven-dried to constant weight A , immersed in water for 24 hr, then surface-dried by the use of a towel and weighed (B). The sample is then placed in a wire basket and its weight in water is determined (C). From the determinations thus made the following values are calculated:

$$\begin{aligned}\text{Bulk Specific Gravity} &= \frac{A}{B - C} \\ \text{Apparent Specific Gravity} &= \frac{A}{A - C} \\ \text{Percentage of Absorption} &= \frac{B - A}{A} \times 100\end{aligned}$$

Still another kind of specific gravity is sometimes obtained, especially for aggregate to be used in concrete; namely, the so-called Bulk Specific Gravity in a Saturated, Surface-dry Condition ($B/B - C$).

SOUNDNESS OF ROCK

By “soundness of rock” is meant its resistance to the weather, generally its resistance to freezing and thawing action. The rapidity of disintegration of rock under the action of freezing and thawing depends upon a number of factors, the principal of which is the extent to which the pores in the rock are saturated with water. If it were possible to thoroughly fill the interior voids in rock, disintegration would occur in a very few cycles of freezing and thawing because of the tremendous internal force exerted by the ice formed in the pores of the rock. On the other hand, if there is not complete saturation, the action is by no means so severe, because incomplete filling of the voids leaves a space

to be occupied by the ice, which then has less disruptive effect. High absorption accompanied by weakness of structure accelerates the disrupting effect of freezing. Apparently the size and shape of the pore structure influence the severity of disruption due to freezing.

In the laboratory, attempts are made to accelerate the action of freezing and thawing by the use of special tests for soundness of the rock. The tests now in general practice are the so-called sodium sulphate and the magnesium sulphate accelerated soundness tests. These tests are fully described in the Standards of the ASTM. Briefly, the sodium sulphate solution is prepared as a saturated solution at 70°F. The previously prepared rock samples are washed, dried, and then immersed in the solution and kept there at a constant temperature for approximately 18 hr. The sample is then removed, dried in an oven at 105° to 110°C, then cooled to room temperature. This cycle of immersion and drying is repeated a number of times as required by the particular specification governing the quality of the rock. Generally, only five cycles are required and the usual limiting percentage of loss is 10. When stone is used in trickling filters for sewage disposal, usually 20 cycles of the sodium sulphate test are required, with a limiting loss of 10 pct. This is a very severe test and many rock samples are rejected. So much in doubt is the value of this test that many specifications, notably those of the Federal Specifications Board, permit the material to be used even though it fails in the test, provided it can be shown that it has a satisfactory service record. The magnesium sulphate test, which is made in the same manner as the sodium sulphate test, is usually the more severe of the two.

Many laboratories also make freezing and thawing tests but the freezing test has not yet been standardized and is performed differently by different laboratories. There seems to be no agreement as to the procedure to be used, whether the sample is to be immersed in water during freezing or is to be thawed in the air or in water at room temperature, or in water at 40°F. A truly indicative accelerated soundness test is much to be desired.

Other special tests are made on stone for use as an aggregate and for other purposes. For illustration, at times the cementing-value test is made to determine the cementing strength of the rock dust formed by attrition. This test is made by grinding the sample with sufficient water to make a paste. This paste is then molded into briquettes 25 mm in diameter and 25 mm high and dried at 100°C. After cooling, the briquettes are subjected to repeated blows by a 1-kg hammer falling 1 cm. The number of blows required to destroy the briquette is taken as a measure of the cementing value. At the present time this test is seldom practiced. Apparently, the cementing value is greatly dependent upon the fineness of the dust produced by attrition. Even rocks that have

relatively low cementing value may have their cementing value increased by finer grinding.

Tests for size and mechanical analysis are made almost universally by the use of square-opening sieves conforming to United States Standard Sieve Sizes. These sieves are fully described in ASTM Standard E 11.

Formerly, round-opening screens were universally used for the measurement of the size of coarse aggregate and square-opening sieves for making sieve tests on fine aggregates. A square-opening sieve is most closely approximated by a round opening having a diameter midway between that of the inscribed and circumscribed circles. Accordingly, the same size of material will be passed through a round screen opening with a diameter of 1.21 times the side of a square opening. This equivalence is approximate, of course.

In making sieving tests of fine aggregate, it is usual to use a series of sieves selected from the U. S. Standard in which the successive openings are in the ratio of 2 to 1. Intermediate sieves are also provided in the series in the ratio of $\sqrt{2}:1$ and $\sqrt[3]{2}:1$. For determining the extremely fine material in either coarse or fine aggregates, it is customary to wash the sample over a No. 200 sieve and to group the material washed through under the general classification of "lost by elutriation."

The term "fineness modulus" is used frequently in connection with sieving tests of aggregates. It is a number determined by adding the cumulative percentages retained on the Nos. 100, 50, 30, 16, 8, 4, $\frac{3}{8}$ -in., $\frac{3}{4}$ -in., $1\frac{1}{2}$ -in., and 3-in. square-opening sieves of the U. S. Standard and dividing this sum by 100. The fineness modulus gives a measure of the general size of the aggregate, although there can be a number of gradations giving the same fineness modulus. Its principal use at the present time is for the control of the uniformity of shipments of fine aggregate for use in concrete. Specifications frequently require that there shall be a variation in fineness modulus of not more than 0.2. Fineness modulus likewise is used in calculations made in the proportioning of concrete.

The question of how a sieve analysis should be expressed is one that has been the subject of controversy due largely to differences in established practice in the different industries in which aggregates are used. For illustration, engineers who deal primarily with bituminous paving mixtures like to think of the gradation of aggregates in terms of the fractional percentage of the entire sample retained on a given sieve, which passes the next larger sieve. Those who deal with concrete, on the other hand, more generally are accustomed to thinking of the mechanical analysis of an aggregate in terms of the total percentages retained on or the total percentages passing the various sieves used for size determination. Unfortunately, it seems to be impossible to convert

a mechanical analysis expressed in terms of the various size fractions into that in which total percentages passing or total percentages retained on the various sieves are used.

For the study of the mechanical analysis of aggregates, a mechanical analysis curve is frequently plotted, generally in terms of total percentages passing used as ordinates and sizes of sieve opening as abscissas. Frequently it is convenient to use a semilogarithmic scale for the size of sieve opening. This results in exaggerating the spacing of the small-size sieves, which are very close together. In the logarithmic plotting of the sieve openings, the abscissas are spaced in proportion to the logarithms of the sieve openings.

STANDARD SIZES OF CRUSHED STONE

Some 20 years ago, specifications for the size of stone for different purposes were written, some in terms of round-opening screens and others in terms of square openings. The sizes required for identically the same purpose varied largely, not only as between maximum and minimum sizes but also in the limits of tolerance permitted on the intermediate screens. In consequence of this wide range of specifications, commercial stone companies were required to stock more sizes than were needed to really meet construction requirements. So an effort was made, initiated largely by the three national aggregate associations, to bring about a simplification and standardization of aggregate sizes throughout the United States. The aid of the Division of Simplified Practice of the National Bureau of Standards was sought and as a consequence there has been evolved a Simplified Practice Recommendation for sizes, which at the present time is designated as R 163-48. It is not expected that this standard will remain constant but that it will be improved as the need becomes apparent. Many of the state highway departments have accepted this standard either in whole or in part and most of the national specifications are now written in terms of this recommendation. Its complete adoption by all local specification-writing bodies would do much toward simplifying the production of crushed stone and would eliminate difficulties in its use. This standard is so important that the sizes recommended are shown in Table 3 and the uses for which these sizes are applicable are given in Table 4.

USES FOR CRUSHED STONE

Crushed stone for the most part is used as an aggregate in highway construction, concrete, railroad ballast, as riprap, in sewage filter beds, as fine aggregate in concrete products and for many other purposes. Limestone and marble are used largely as fluxstone in smelting, in the manufacture of cement, for lime, in sugar manufacture, in rock wool, for agricultural limestone, in the chemical industries and glass

TABLE 3—*Sizes of Coarse Aggregates (Crushed Stone, Gravel, and Slag)*
Simplified Practice Recommendation R 163-48

Size No.	Nominal Size Square Openings ^a	Amounts Finer than Each Laboratory Sieve (Square Openings), Percentage by Weight									
		4	3½	3	2½	2	1½	1	¾	½	⅜
1	3½-1½	100	90-100		25-60		0-15		0-5		
1-F ^b	3½-2	100	90-100			0-10	0-9	0-2			
2	3-1½		100	90-100	90-100	35-70	0-15		0-5		
2-F ^b	3-1½		100	100	90-100	95-100	25-60	0-15	0-10	0-5	
3	2½-1				100	95-100	35-70	0-15			
3-F ^b	2½-1				100	100	95-100	35-70		0-5	
4	2-¾					100	90-100	20-55			
4-F ^b	2-¾					100	95-100	20-55			
5	1½-¾					100	90-100	0-5	0-5		
5-F ^b	1½-¾					100	90-100	0-5	0-5		
6	1-¾					100	90-100	0-5	0-5		
6-F ^b	1-¾					100	90-100	0-5	0-5		
7	1-¾					100	90-100	0-5	0-5		
7-F ^b	1-¾					100	90-100	0-5	0-5		
8	1-¾					100	90-100	0-5	0-5		
8-F ^b	1-¾					100	90-100	0-5	0-5		
9	1-¾					100	90-100	0-5	0-5		
9-F ^b	1-¾					100	90-100	0-5	0-5		
10	1-¾					100	90-100	0-5	0-5		
10-F ^b	1-¾					100	90-100	0-5	0-5		
11	1-¾					100	90-100	0-5	0-5		
11-F ^b	1-¾					100	90-100	0-5	0-5		
12	1-¾					100	90-100	0-5	0-5		
12-F ^b	1-¾					100	90-100	0-5	0-5		
13	1-¾					100	90-100	0-5	0-5		
13-F ^b	1-¾					100	90-100	0-5	0-5		
14	1-¾					100	90-100	0-5	0-5		
14-F ^b	1-¾					100	90-100	0-5	0-5		
15	1-¾					100	90-100	0-5	0-5		
15-F ^b	1-¾					100	90-100	0-5	0-5		
16	1-¾					100	90-100	0-5	0-5		
16-F ^b	1-¾					100	90-100	0-5	0-5		
17	1-¾					100	90-100	0-5	0-5		
17-F ^b	1-¾					100	90-100	0-5	0-5		
18	1-¾					100	90-100	0-5	0-5		
18-F ^b	1-¾					100	90-100	0-5	0-5		
19	1-¾					100	90-100	0-5	0-5		
19-F ^b	1-¾					100	90-100	0-5	0-5		
20	1-¾					100	90-100	0-5	0-5		
20-F ^b	1-¾					100	90-100	0-5	0-5		
21	1-¾					100	90-100	0-5	0-5		
21-F ^b	1-¾					100	90-100	0-5	0-5		
22	1-¾					100	90-100	0-5	0-5		
22-F ^b	1-¾					100	90-100	0-5	0-5		
23	1-¾					100	90-100	0-5	0-5		
23-F ^b	1-¾					100	90-100	0-5	0-5		
24	1-¾					100	90-100	0-5	0-5		
24-F ^b	1-¾					100	90-100	0-5	0-5		
25	1-¾					100	90-100	0-5	0-5		
25-F ^b	1-¾					100	90-100	0-5	0-5		
26	1-¾					100	90-100	0-5	0-5		
26-F ^b	1-¾					100	90-100	0-5	0-5		
27	1-¾					100	90-100	0-5	0-5		
27-F ^b	1-¾					100	90-100	0-5	0-5		
28	1-¾					100	90-100	0-5	0-5		
28-F ^b	1-¾					100	90-100	0-5	0-5		
29	1-¾					100	90-100	0-5	0-5		
29-F ^b	1-¾					100	90-100	0-5	0-5		
30	1-¾					100	90-100	0-5	0-5		
30-F ^b	1-¾					100	90-100	0-5	0-5		
31	1-¾					100	90-100	0-5	0-5		
31-F ^b	1-¾					100	90-100	0-5	0-5		
32	1-¾					100	90-100	0-5	0-5		
32-F ^b	1-¾					100	90-100	0-5	0-5		
33	1-¾					100	90-100	0-5	0-5		
33-F ^b	1-¾					100	90-100	0-5	0-5		
34	1-¾					100	90-100	0-5	0-5		
34-F ^b	1-¾					100	90-100	0-5	0-5		
35	1-¾					100	90-100	0-5	0-5		
35-F ^b	1-¾					100	90-100	0-5	0-5		
36	1-¾					100	90-100	0-5	0-5		
36-F ^b	1-¾					100	90-100	0-5	0-5		
37	1-¾					100	90-100	0-5	0-5		
37-F ^b	1-¾					100	90-100	0-5	0-5		
38	1-¾					100	90-100	0-5	0-5		
38-F ^b	1-¾					100	90-100	0-5	0-5		
39	1-¾					100	90-100	0-5	0-5		
39-F ^b	1-¾					100	90-100	0-5	0-5		
40	1-¾					100	90-100	0-5	0-5		
40-F ^b	1-¾					100	90-100	0-5	0-5		
41	1-¾					100	90-100	0-5	0-5		
41-F ^b	1-¾					100	90-100	0-5	0-5		
42	1-¾					100	90-100	0-5	0-5		
42-F ^b	1-¾					100	90-100	0-5	0-5		
43	1-¾					100	90-100	0-5	0-5		
43-F ^b	1-¾					100	90-100	0-5	0-5		
44	1-¾					100	90-100	0-5	0-5		
44-F ^b	1-¾					100	90-100	0-5	0-5		
45	1-¾					100	90-100	0-5	0-5		
45-F ^b	1-¾					100	90-100	0-5	0-5		
46	1-¾					100	90-100	0-5	0-5		
46-F ^b	1-¾					100	90-100	0-5	0-5		
47	1-¾					100	90-100	0-5	0-5		
47-F ^b	1-¾					100	90-100	0-5	0-5		
48	1-¾					100	90-100	0-5	0-5		
48-F ^b	1-¾					100	90-100	0-5	0-5		
49	1-¾					100	90-100	0-5	0-5		
49-F ^b	1-¾					100	90-100	0-5	0-5		
50	1-¾					100	90-100	0-5	0-5		
50-F ^b	1-¾					100	90-100	0-5	0-5		
51	1-¾					100	90-100	0-5	0-5		
51-F ^b	1-¾					100	90-100	0-5	0-5		
52	1-¾					100	90-100	0-5	0-5		
52-F ^b	1-¾					100	90-100	0-5	0-5		
53	1-¾					100	90-100	0-5	0-5		
53-F ^b	1-¾					100	90-100	0-5	0-5		
54	1-¾					100	90-100	0-5	0-5		
54-F ^b	1-¾					100	90-100	0-5	0-5		
55	1-¾					100	90-100	0-5	0-5		
55-F ^b	1-¾					100	90-100	0-5	0-5		
56	1-¾					100	90-100	0-5	0-5		
56-F ^b	1-¾					100	90-100	0-5	0-5		
57	1-¾					100	90-100	0-5	0-5		
57-F ^b	1-¾					100	90-100	0-5	0-5		
58	1-¾					100	90-100	0-5	0-5		
58-F ^b	1-¾					100	90-100	0-5	0-5		
59	1-¾					100	90-100	0-5	0-5		
59-F ^b	1-¾					100	90-100	0-5	0-5		
60	1-¾					100	90-100	0-5	0-5		
60-F ^b	1-¾					100	90-100	0-5	0-5		
61	1-¾					100	90-100	0-5	0-5		
61-F ^b	1-¾					100	90-100	0-5	0-5		
62	1-¾					100	90-100	0-5	0-5		
62-F ^b	1-¾					100	90-100	0-5	0-5		
63	1-¾					100	90-100	0-5	0-5		
63-F ^b	1-¾					100	90-100	0-5	0-5		
64	1-¾					100	90-100	0-5	0-5		
64-F ^b	1-¾					100	90-100	0-5	0-5		
65	1-¾					100	90-100	0-5	0-5		
65-F ^b	1-¾					100	90-100	0-5	0-5		
66	1-¾					100	90-100	0-5	0-5		
66-F ^b	1-¾					100	90-100	0-5	0-5		
67	1-¾					100	90-100	0-5	0-5		
67-F ^b	1-¾					100	90-100	0-5	0-5		
68	1-¾					100	90-100	0-5	0-5		
68-F ^b	1-¾					100	90-100	0-5	0-5		
69	1-¾					100	90-100	0-5	0-5		
69-F ^b	1-¾					100	90-100	0-5	0-5		
70	1-¾					100	90-100	0-5	0-5		
70-F ^b	1-¾					100	90-100	0-5	0-5		
71	1-¾					100	90-100	0-5	0-5		
71-F ^b	1-¾					100	90-100	0-5	0-5		
72	1-¾					100	90-100	0-5	0-5		
72-F ^b	1-¾					100	90-100</				

TABLE 4—Typical Uses for Sizes Shown in Table 3

Use	Size Number and Nominal Size ^a														
	1	1-F	2-F	2	2 1/2	3	3 1/2	4	4 1/2	5	5 1/2	6	6 1/2	7	7 1/2
Water-bound macadam:															
Coarse aggregate.....	3 1/2 to 1 1/2	3 1/2 to 1 1/2	3 1/2 to 1 1/2	2 1/2 to 1 1/2	2 1/2 to 1 1/2	2 to 1	2 to 1 1/2	1 1/2 to 1 1/2	1 1/2 to 1 1/2	1 to 1 1/2	1 to 1 1/2	3/4 to 1 1/2	3/4 to 1 1/2	1/2 to 1 1/2	1/2 to 1 1/2
Filler.....															
Bituminous macadam, penetration method:															
Coarse aggregate.....															
Choke.....															
Seal.....															
Bituminous plant mixes, base or surface courses: ^b															
Base, open mix.....															
Base, closed mix.....															
Binder course.....															
Surface course, coarse grading.....															
Surface course, fine grading.....															
Seal.....															
Bituminous road mix:															
Mixing course.....															
Choke.....															
Seal.....															
Drag leveling course:															
Leveling course.....															
Seal.....															
Bituminous surface treatment.....															
Seal for airport construction.....															
Portland cement concrete.....															
Railroad ballast:															
Stone or slag.....															
Gravel.....															
Roading.....															
Sewage trickling filter media.....															

^a In inches, except where otherwise indicated. Numbered sieves are those of the United States Standard Sieve Series.

^b For plant mixes the aggregate should consist of appropriate sizes selected from Table 3 combined with suitably graded fine aggregate.

^c Bottom course of multiple surface treatment.

manufacture and as filler for various purposes, including bituminous road mixtures, and in the form of dust for the rock-dusting of coal mines to render them less subject to explosions.

Concrete and Road Metal

Rocks of many different kinds, provided they are sufficiently strong and durable, are used in highway construction in various ways. Crushed stone is used as the coarse aggregate and frequently as the fine aggregate in concrete for pavements. It is used as the road metal for macadam bases and in the so-called traffic-bound type of base, as an aggregate in bituminous macadam, bituminous concrete and bituminous mixtures of the road-mix type, and as cover stone for bituminous surfaced roads, usually, in that case, in the form of small-sized material extending from approximately $\frac{1}{2}$ in. to the No. 8 sieve size or smaller.

Stone is a low-cost commodity and as a rule it is not shipped by truck much more than 30 miles and by railroad not much more than 100 miles. Consequently, it is used locally and, accordingly, the specifications for quality of crushed stone differ in different states, depending upon the economic availability of stone suitable for use. Generally national specifications such as those of the Federal Specifications Board, the American Society for Testing Materials, and others are written in terms of the least acceptable quality, whereas local specifications are more likely to require stone of a higher quality if such stone exists locally. It is readily apparent, therefore, why the specifications for quality of stone for different purposes vary somewhat throughout the United States. National specifications rather generally require that the stone have the following limiting percentage of wear in the Los Angeles abrasion test for the various purposes listed:

USE	PCT
Portland cement concrete base course, generally.....	50-60
Waterbound macadam base.....	60
Surface course.....	40
Bituminous macadam base.....	50
Surface.....	40
Bituminous concrete base.....	50
Surface.....	40
Concrete surface course, generally.....	40

Concrete

Characteristics desirable in crushed stone for use in concrete depend greatly upon the kind of structure to be built. The coarse aggregate in concrete serves as a filling material, thereby reducing the quantity of cement necessary per cubic yard and, because of its effect in reducing the cement, it serves to impart to the concrete the property of minimum shrinkage, since the volume change in concrete due to the drying out

of the moisture is attributable primarily to the cement. Accordingly, it is desirable that the coarse aggregate occupy as great a volume of the concrete mass as possible commensurate with the necessary degree of concrete workability. Too much coarse aggregate produces excessively harsh working concrete. Too little coarse aggregate requires oversanding of the mix, which in turn results in too much mixing water and excessive shrinkage.

The maximum size of coarse aggregate usually is selected on the basis of the design of the structure to be built. For illustration, thin members with a great deal of closely spaced reinforcing steel require a small-size coarse aggregate, while, on the other hand, for economy, mass concrete requires the use of very large-size coarse aggregate. In the Hoover Dam, for instance, the maximum size of coarse aggregate was 9 in. although $\frac{3}{4}$ -in. maximum size is quite usual for reinforced-concrete construction. In highways, a maximum size of from $1\frac{1}{2}$ to $2\frac{1}{2}$ in. is quite customary.

The physical properties desired in coarse aggregate depend upon the kind of structure and the service it must render. It is very important that the coarse aggregate be sound for structures exposed to the weather, whereas this property is not so important in unexposed structures. As a rule, most commercial coarse aggregates have sufficient strength, as measured by the usual physical tests, to serve their purpose satisfactorily. It is a fact that the strength of the concrete is affected to some extent by the strength of the coarse aggregate; the higher the percentage of wear in the Los Angeles abrasion test made on the coarse aggregate, the lower the beam strength is apt to be, and this becomes important in aggregates for use in highway construction or in other types of structures in which resistance to bending is important. In structures such as dams, exposed to water action, great attention must be paid to the chemical characteristics of the aggregate, particularly if there is likely to be interaction between the silica in the aggregate and the cement having a high alkali content. Although limestones are very slowly soluble in water, investigations have shown that limestone aggregates give excellent service in structures exposed to long-continued water action. If there is any corrosion of the surface, it almost invariably takes place in the mortar rather than in the coarse aggregate because of the higher solubility of the hardened portland cement paste.

Stone for use in asphaltic concrete sometimes gives variable results depending upon the affinity of the stone for the asphalt. In general, highly acidic types of rocks have a much higher affinity for water than for asphalt; consequently, when asphaltic mixtures of that type are exposed to long-continued water action, the asphalt may become displaced by the water and failure of the mixture is apt to ensue. Rocks of this type have been classed as hydrophilic—they like water—while rocks

exhibiting a better adhesion for asphalt are classed as hydrophobic. This distinction is not very clearcut but it is a fact that asphaltic mixtures made with different types of rocks show different degrees of durability upon long exposure to the water. Much research has been done on additives for use with asphalt or for treating the surface of aggregates for the purpose of overcoming this so-called stripping difficulty. The binder course underlying the surface course in a pavement is most apt to lose its asphaltic film.

The fire-resistant qualities of aggregates for use in building concrete structures are important. Limestone and trap rock are both excellent aggregates for this purpose while highly siliceous aggregates, particularly chert, are not so desirable because of their tendency to cause spalling of the concrete during times of high temperature. When spalling takes place, the underlying structural steel or reinforcing steel is exposed to the heat and, since the yield point of steel is very greatly reduced even by moderate heat, the structure is very likely to fail. Not enough attention is paid to the fire-resistant qualities of aggregates.

Railroad Ballast

The American Railway Engineering Association has issued a specification for stone for use as railroad ballast and, although formerly stone ballast of $\frac{3}{4}$ to $2\frac{1}{2}$ -in. size was almost universally used, the tendency nowadays is to use a number of smaller sizes; for instance, sizes Nos. 3, 4, 5, and 57 in Table 3 now appear in the AREA specifications. The tools used to tamp the ballast under the ties in maintenance operations impart a severe blow to the ballast and it should be resistant to this kind of action. At the present time the AREA permits a ballast having as high as 40 pct of wear in the Los Angeles abrasion test. This, however, is the maximum permissible limit and the lower the percentage of wear, the more resistant the ballast is apt to be. The angularity of broken stone makes for very high stability and it is for this reason that stone ballast is so highly regarded.

Sewage Filter Beds

Crushed stone is used in rather large quantities for trickling or sprinkling filters in sewage-treatment plants. It is necessary that there be a high percentage of voids in the stone used for this purpose, so that the bed will remain free from clogging. It also seems desirable that the voids be rather large in size, for otherwise, although the percentage of voids might be high when the bed is new, the building up of a bacterial gel on the surface of the stone soon tends to greatly reduce the percentage of voids in small-sized material. For a standard filter bed, a good size seems to be from $1\frac{1}{2}$ to $2\frac{1}{2}$ in. with small tolerances on the upper and lower sizes. For high-rate filters, the size is increased, extending

from 2 to 3 in. Unusual care must be taken in the preparation of the stone for trickling filters. At the present time, it is generally required that the stone show satisfactory soundness after 20 cycles of the sodium sulphate soundness test. This is an unusually severe test and the consequence is that in many localities it is difficult to get material locally. It must then be shipped from long distances at high cost for transportation. There is well-founded doubt as to whether the sodium sulphate test as now made on trickling-filter stone is entirely satisfactory for that purpose and investigations are needed to reexamine the appropriateness of the test as now made.

Stone Sand

The fine material resulting from the crushing operation is processed in many plants to produce a fine aggregate for use in concrete and in bituminous mixtures. Excessive 100-mesh dust is removed, generally by some form of washing process, and the fines are regraded to form a satisfactory sand gradation. All stone screenings are not equally suitable for making stone sand, because of their particle shape. Some screenings, because of their method of preparation and the characteristics of the material, contain many flat and extremely elongated pieces, and sand made from such material is apt to produce harsh working concrete. When the percentage of silica is low, as in many limestones and dolomites, an impact type of crusher is used for the preparation of stone sand. Rod mills and ring rolls and also the roll type of crusher are used for producing stone sand of very satisfactory particle shape. In general, it is undesirable to have the maximum size of stone sand greater than that which will pass a No. 8 sieve. Likewise, for the sake of workability, it is well to have at least 15 pct of the particles passing a No. 50 sieve with as high as 8 to 10 pct through a No. 100 sieve. Above all, the sand should be sound. The use of air-entraining agents in concrete has done much toward improving the quality of stone-sand concrete. Stone sands that formerly were somewhat harsh-working can be used with great satisfaction when an air-entraining agent is utilized in the concrete and the durability of the concrete is greatly improved.

Fluxstone

Limestone is used as a fluxing agent in the smelting and refining of iron and other metals. It combines with the silica and alumina of the ore, fuel or metal to form a readily fusible slag, which in its fluid state separates from the metal because of the difference in specific gravity of the fluid metal and fluid slag. The slag and the metal may then be tapped from the furnace separately. For use in the iron blast furnace, stone of roughly 1 to 4-in. size is used, the preference being for somewhat closer sizing. With lump ores, a size similar to that to which the ore is prepared, usually 2 to 3 in., gives the most uniform mix in

the charge. With fine ores, a size producing maximum porosity is desirable, to permit the easier passage of the gases through the furnace column. Stone should be of sufficient strength to withstand the heavy burden of the high column of ore and should resist decrepitation due to intense heat. Certain marbles are unsuitable because they decrepitate to a powder under the heat of the furnace. Silica in the flux is undesirable because the available basic elements in the flux are thus reduced and the heat supply does a smaller amount of useful work. Blast furnaces can use flux with a somewhat higher silica content than can open-hearth furnaces. For a blast furnace, the silica may at times extend as high as 5 pct if the available supply and relative cost of the stone make this permissible, but generally it is desirable that the silica should not exceed 1.5 pct.

Specifications for fluxstone for foundry cupola use are about the same as for furnace use, although a smaller size is used, usually about $1\frac{1}{2}$ to 2 in. High-calcium stone is generally desired but dolomitic stone is used occasionally. To increase the slag volume, siliceous stone is employed.

In the basic open-hearth steel process, a high-calcium limestone low in silica, sulphur, and phosphorus is necessary. High calcium is needed to reduce the phosphorus in the steel and carry it into the slag. Silica is more detrimental in the open-hearth furnace than in the blast furnace because open-hearth slags are more basic than blast-furnace slags and the presence of silica reduces the amount of the available lime.

In copper and lead smelting, limestone is used as a flux when the ores run more acid than basic. When the copper ores are basic, they require silica as the fluxing agent, but as a rule siliceous ores can be obtained to provide a self-fluxing mix and obviate the necessity for fine silica.

Portland Cement, Lime, and Rock Wool

The raw materials for cement manufacture, their quarrying and preparation, are covered in the chapter on Cement. Sometimes limestone is purchased to raise the lime content. This material must be high in lime and low in magnesia.

The quality of limestone used in the burning of lime is dependent upon the use for which the lime is intended. The manufacture of lime is an industry in itself and is covered in the chapter on Lime.

Rock wool is one of the important insulating materials used in building construction. The details of the raw materials employed, the methods of manufacture and the uses for rock wool are covered in the chapter on Heat and Sound Insulating Materials.

Sugar Manufacture

In the manufacture of sugar, lime is added to the juice of the cane or beets to neutralize the free acids. It is then precipitated with carbon

dioxide gas and in settling it carries the colloidal matter with it and clarifies the liquor. As the manufacturer uses both lime and carbon dioxide, he usually buys the raw limestone and burns it himself. High-calcium stone containing about 97 pct of calcium carbonate free from impurities that would impart a taste is required.

Agricultural Limestone

The soil conservation program of the United States Department of Agriculture has given great impetus to the use of agricultural limestone. Limestone and dolomitic limestone furnish the important elements of calcium and magnesium necessary for the correction of acidity of the soil and for the promotion of plant life. Its action apparently extends further than that of a mere neutralizer for acidity, and, according to some agronomists, it likewise makes readily available certain other mineral soil constituents needed for the stimulation of plant growth and the building up of the soil. Limestone in its finely divided state slowly goes into solution, the finer particles becoming available first and the coarser particles dissolving at a slower rate, thus prolonging the neutralizing action. The particle-size gradation of agricultural limestone is not constant throughout the country; in some sections, finely ground dust is used while in other sections the gradation may extend from material passing the No. 4 sieve down to dust.

Chemical Industries

In the chapter on Lime many uses for lime in the chemical industry are listed. The raw limestone is the basic product from which the lime is manufactured. The finer sizes of limestone are used for the neutralization of acid wastes; sometimes it is pulverized and sometimes it is used in the form of fines from the No. 8 to the No. 4 sieves, without dust, so as to provide free percolation for the acid solution to be neutralized.

Glass

Limestone is an essential ingredient in the manufacture of glass of different kinds, including flint, plate, window and bottle glass. High-calcium limestone is required. Relative freedom from iron is essential; for most glass, the iron content should not exceed 0.3 pct and for flint glass it should be not over 0.03 pct. Organic matter likewise is limited to about 0.3 pct. The size required is usually from 20 to 100-mesh, so as to permit its intimate mixture with silica of about the same gradation.

Fillers

Limestone is one of the important inert fillers used either to fill voids, add weight, or impart color. The fineness varies, depending upon the use to which the filler is put. For asphalt pavements, limestone dust is one

of the most widely used of all mineral fillers. Roughly, about the same percentage by weight of filler is used as of asphalt in the mixture. The limestone filler toughens the mixture, tends to give it stability, and renders it less susceptible to the effect of changes in temperature. The Federal Specifications for Mineral Fillers require the use of limestone or dolomite dust or portland cement having 100 pct through the No. 30 sieve and 65 to 100 pct through the No. 200 sieve. Other specifications require 85 pct to pass the No. 200 sieve.

When a very white filler is required, either pulverized limestone, marble, precipitated calcium carbonate, or chalk is generally used. This material is termed "whiting" and originally was manufactured from pulverized chalk (see chapter on Chalk). All limestone deposits do not yield an equally suitable substitute for whiting and its characteristics should be determined by test prior to its manufacture for this purpose. Whiting is used for cold-water paints, putty, calcimine, as a component of glazes, enamels and fluxed ceramic materials. It is used also as a filler in rubber, oilcloth, linoleum and cigarette paper and as a coating on glazed paper, in white shoe dressing, white ink, dyes, toothpaste, and many other articles.

Rock Dusting

The use of finely pulverized rock for the dusting of bituminous coal mines has become recognized as one of the most effective methods for reducing and preventing the spread of mine explosions. Limestone dust for this purpose should be light in color, free as possible of carbonaceous matter and relatively free from silica. A low silica content in the dust is desirable as a precaution against silicosis. The light color aids in judging the percentage of dust added in the mixture with coal dust and increases the illumination in the mine. The Bureau of Mines requires that dust for the rock dusting of mines have not more than 5 pct of combustible matter nor more than 25 pct of quartz or free silica. All of the dust must pass through a No. 20 sieve and 60 pct or more must pass through a sieve having 200 mesh openings per linear inch.

PRODUCTION AND CONSUMPTION

Crushed stone is a low-priced commodity and consequently most of it is shipped as it is produced, without stock piling. Some of it is stockpiled, however, to meet future demands and to provide for the variation in demands for different sizes. There is not much variation in the total stocks carried, although the stock piles are apt to be larger at the beginning of a construction season. There is very little difference in the tonnage of stone produced and consumed during the year.

In Table 5 is given the production of crushed and broken stone in the United States classified as to uses. The kinds of crushed stone sold or used by producers in the United States in 1946 for concrete, road metal, and railroad ballast are given in Table 6.

TABLE 5—Crushed and Broken Stone Sold or Used by Producers in the United States, 1945-1946, by Principal Uses^a

Use	1945			1946		
	Short Tons	Value		Short Tons	Value	
		Total	Average		Total	Average
Concrete and road metal.....	64,108,190	\$65,535,403	\$1.02	90,358,900	\$97,765,446	\$1.08
Railroad ballast.....	21,265,070	14,894,216	0.70	16,908,350	13,127,058	0.78
Furnace flux (limestone).....	27,639,520	22,076,393	0.80	25,157,760	20,791,833	0.83
Agricultural (limestone).....	17,395,570	25,892,317	1.49	22,781,750	32,482,907	1.43
Alkali works.....	7,076,330	4,068,060	0.57	7,418,690	5,230,804	0.71
Riprap.....	4,801,170	5,589,584	1.16	3,847,550	5,010,207	1.30
Refractory stone ^b	2,526,650	4,545,339	1.80	2,088,080	4,157,179	1.99
Asphalt filler.....	455,360	971,570	2.13	459,020	1,270,734	2.77
Calcium carbide works.....	549,510	639,833	1.16	411,660	437,231	1.06
Sugar factories.....	340,310 ^c	691,922 ^c	2.03	378,720	693,058	1.83
Glass factories.....	556,610 ^c	937,615 ^c	1.68	648,250	1,163,161	1.79
Paper mills.....	352,990	620,943	1.76	385,620	683,912	1.78
Other uses.....	5,279,240	14,996,069	2.84	6,633,430	18,551,736	2.80
Portland cement (including "cement rock").....	152,346,520	\$161,459,264	\$1.06	177,477,780	\$201,367,266	\$1.13
Natural cement ("cement rock").....	27,332,000	^d		43,877,000	^a	
Lime.....	11,841,000	^d		11,985,000	^d	
Total.....	191,520,000	^d		233,340,000	^d	

^a Compiled by the U. S. Bureau of Mines.^b Gneiss (sandstone), mica schist, dolomite, and soapstone.^c Revised figure.^d No value available for stone used in manufacture of cement and lime.

Commercial and Noncommercial Stone Production—All crushed stone is not produced by commercial operations and the extent of the noncommercial production varies from year to year, depending upon economic conditions. For several years prior to 1940, noncommercial production, principally Government-sponsored enterprises, produced 29 to 46 pct of the total output. During the war, a radical change in the percentage of noncommercial production took place because unemployment was no longer a problem. Noncommercial production dropped to only 9 pct of the total in 1943, increased to 12 pct in 1944, and in 1945 accounted for only 7 pct of the total production.

Sizes of Crushed-stone Plants—The plants producing crushed stone vary greatly in size. The general trend has been toward an increase in the number of plants in the larger size groups and a larger percentage of the total production by those groups. For illustration, in 1941 there were 41 plants producing 500,000 tons or more per year and they pro-

TABLE 6—*Crushed and Broken Stone Sold or Used by Producers in the United States in 1946, by Kinds^a*

Kind	Concrete and Road Metal			Railroad Ballast		
	Short Tons	Value		Short Tons	Value	
		Total	Average		Total	Average
Granite.....	6,803,850	\$8,465,073	\$1.24	2,354,050	\$2,403,249	\$1.02
Basalt.....	12,863,090	16,101,322	1.25	2,530,110	2,429,099	0.96
Marble.....						
Limestone.....	62,270,570	66,307,005	1.06	7,330,420	6,083,202	0.83
Sandstone.....	1,716,400	1,830,536	1.07	269,790	315,075	1.17
Misc. stone ^b	6,704,990	5,061,510	0.75	4,423,980	1,896,433	0.43
	90,358,900	\$97,765,446	\$1.08	16,908,350	\$13,127,058	\$0.78

^a Compiled by the U. S. Bureau of Mines.

^b Includes soapstone; mica schist, volcanic rock, argillite, and other varieties that cannot be classified in the principal groups.

duced 34 pct of the total. During the three following years, there were 51 to 61 plants in that size range and they produced 40 to 41 pct of the total stone tonnage. Table 7 shows the number and production of commercial crushed-stone plants in 1944 and 1945 by sizes of output.

Methods of Transportation—Because stone is a low-cost commodity, it is used locally for the most part. The maximum haul by truck probably seldom exceeds 30 miles, while the maximum haul by rail is not much more than 100 miles. In 1945, roughly 62 pct of the tonnage was hauled by truck, 30 pct by rail, 4 pct by waterway, and 4 pct was unspecified.

PROSPECTING

Before initiating a quarrying operation, it is essential that the deposit be prospected to determine the quality of the stone, estimate the quantity, design the layout of the quarry and plant, and locate the area for the disposal of wastes in a desirable position, so that it will not cover usable stone. Thorough prospecting is highly essential, for the margin of profit in the sale of crushed stone is so low that unforeseen costs may be fatal to the success of the undertaking. As a rule, igneous deposits are uniform in quality and covered with thin overburden and, because of their uniformity, surface sampling is sometimes adequate. Weathering, however, may create inferior rock and faults or other major rock structures that may exist in these will be revealed by proper drilling.

Limestones in some localities are nonuniform in character, are dis-

TABLE 7—*Number and Production of Commercial Crushed-stone^a Plants in 1944-1945, by Sizes of Output^b*

Range of Output, Tons	1944				1945			
	Num- ber of Plants	Total Pro- duction of Plants, Short Tons	Per- cent- age of Total	Cumulative Total, Short Tons	Num- ber of Plants	Total Pro- duction of Plants, Short Tons	Per- cent- age of Total	Cumulative Total, Short Tons
Less than 1,000.....	93	43,330	0.03	43,330	80	36,290	0.02	36,290
1,000-25,000.....	628	6,401,980	4.40	6,445,310	607	6,234,740	4.29	6,271,030
25,000-50,000.....	250	8,788,700	6.04	15,234,010	242	8,537,230	5.88	14,808,260
50,000-75,000.....	141	8,673,570	5.96	23,907,580	135	8,262,000	5.69	23,070,260
75,000-100,000.....	84	7,282,550	5.01	31,190,130	73	6,329,930	4.36	29,400,190
100,000-200,000.....	155	22,333,290	15.36	53,523,420	165	23,279,060	16.03	52,679,250
200,000-300,000.....	67	16,309,320	11.21	69,832,740	67	16,664,430	11.47	69,343,680
300,000-400,000.....	26	8,996,800	6.19	78,829,540	29	9,837,540	6.77	79,181,220
400,000-500,000.....	16	7,166,810	4.93	85,996,350	22	9,839,090	6.77	89,020,310
500,000-600,000.....	13	7,138,200	4.91	93,134,550	11	5,923,690	4.08	94,944,000
600,000-700,000.....	7	4,610,650	3.17	97,745,200	10	6,354,620	4.38	101,298,620
700,000-800,000.....	6	4,592,430	3.16	102,337,630	5	3,710,640	2.56	105,009,260
800,000-900,000.....	3	2,578,290	1.77	104,915,920	5	4,163,060	2.87	109,172,320
900,000 and over....	22	40,516,940	27.86	145,432,860	19	36,062,720	24.83	145,235,040
Total.....	1,511	145,432,860	100.00	145,432,860	1,470	145,235,040	100.00	145,235,040

^a Exclusive of marble, which is primarily a dimension-stone industry.^b Compiled by the U. S. Bureau of Mines.

torted by folds and faults, and may have a considerable overburden. Consequently, thorough drilling in such deposits is advisable.

A map showing the topography, location of roads and railroads, and a geological sketch made from sampling the outcrops and plotting the dips and strikes is a first requirement. State and federal geological reports may furnish valuable information. Near-by quarries should be studied. Such preliminary studies should be made before drilling.

Prospect drilling is done by the well drill, churn drill, and core drill. The well drill breaks up the rock into such small pieces that physical tests are not possible but an experienced driller can estimate the hardness of the rock from the sound of the drill and the speed of drilling. If there are clay seams in the rock, the well-drill samples become unreliable for chemical tests unless casing is used, because clay washes into the hole and the sample thus becomes contaminated.

The well drill furnishes a good means for testing the overburden. For this purpose a hand augur is often used, but it is too easily stopped, even by a small boulder. The well drill, on the other hand, may be used to definitely determine the depth of the solid rock. The well drill serves as a good auxiliary to the core drill. In pitched strata, covered by considerable overburden, the general location of the desired formation can be determined and core-drill holes can thereby be better located, thus saving cost in this more expensive type of drilling.

Two types of core drills are used, the shot drill and the diamond drill. In shot-drill work, chilled steel shot is fed under the tubular bit, together with wash water. The shot serves as the cutting agent and the fine particles of stone are carried away by the wash water. If large seams are encountered, the shot may be lost, and if this happens the seam must be cemented. The diamond drill is better suited for drilling seamy rock but there may be difficulty with the diamond drill entering a smooth surface at an acute angle after passing a seam. If this happens, cementing may be necessary.

In diamond drilling, the black, opaque, minutely crystalline carbonados (carbons) are better suited than the imperfect or colored crystal diamonds (bort), for their lack of cleavage makes them less liable to chip. Because of the increased cost of diamonds, setting the bit with a greater number of smaller stones is being practiced, and there is now available a bit in which the diamonds and powdered metal are compressed to form the crown of a bit. Hard alloys may be substituted for diamonds in drilling the softer rocks.

Rarely is the entire core recovered, because of seams and the wear of sections of the core, one upon the other. On the average, about 70 pct of the entire length of the hole is recoverable as a core. In massive formation or flat strata, the holes may be drilled at the corners of equal squares 50 or 100 ft on a side, or more, depending upon the uniformity of the rock. In drilling pitched strata, it is well to work on cross sections at right angles to the general strike. Well-drill holes must be vertical but diamond-drill holes may be drilled at any angle, and should be, as nearly as practicable, perpendicular to the pitch.

Well-drill bits are commonly $5\frac{5}{8}$ in. in diameter although other sizes are used up to about 9 in. The cost of drilling varies with the type of rock, from roughly something over \$0.50 for a 6-in. hole in dolomite to something over \$3.50 for a $6\frac{3}{8}$ -in. hole in diorite. Diamond-drill cores from $\frac{3}{4}$ to 3 in. in diameter may cost roughly two to three times the cost of well-drill holes. The shot drill may be used for drilling up to 60 in. in diameter and even larger holes have been drilled for the foundations of structures.

Geophysical methods for examining subsurface formations have been applied to the estimation of quarry overburden and the depth down to solid rock. Both electrical resistivity and seismic methods have been used.

STRIPPING

There are very few areas that are not covered with some overburden, which must be stripped from the surface before quarrying can be done. At a few places where the overburden is shallow and consists of friable soil, the stone is shot down together with the overburden, which is then removed by a washing process.

Hand stripping of overburden is seldom practiced today, in view of the high cost of labor and the development of extremely efficient earth-handling equipment.

Hydraulicking—Hydraulic methods of stripping are used where the conditions are favorable. Very seldom, however, do all of the necessary conditions exist for the stripping of quarries by hydraulic methods. From 1500 to 2000 gal of water is required for each cubic yard of overburden to be moved. The slope should be away from the quarry face, otherwise the entire area must be stripped before the quarrying operations commence. The slope must be steep enough to give water in the slough or channel sufficient velocity to carry away the larger solid material. Geike states that 40 fpm is the velocity of water for removing coarse sand and up to 180 fpm for pebbles of egg size. Boulders must be broken up and removed by hand. To avoid stream pollution, a large spoil area is necessary. If such an area is not available close at hand and at a lower level than the soil being removed, the debris can be carried to a sump and pumped by centrifugal dredging pump, but this is an expensive operation. Hydraulic stripping has been used in a number of quarries, usually in areas having rough topography. Such methods cost from 5 to 20¢ per cubic yard.

Power Shovels—Power shovels frequently are used for machine stripping. The cost is low and the same shovels can be used for loading stone in the quarry. Frequently, also, stripping can be done during the winter or other idle period of quarry operation and thus make the purchase of additional equipment unnecessary. Shovels can dig tough clay and inferior rock; they cannot, however, clean out seams, and in many limestone quarries the rock surface is rough and cavities filled with clay extend to considerable depths. For cleaning out pockets, a pull shovel boom may be attached to a small shovel and used as a hoe. A power shovel may be equipped with a dragline boom and bucket and can strip irregular surfaces and clean out vertical seams if they are wide enough to admit the bucket. Where the overburden is deep, it pays to do the stripping in two separate operations; first, a level cut just clearing the peaks of the rock with shovel equipped with dipper, then the remainder with dragline equipment.

Power Scrapers—There has been a remarkable development in handling equipment of recent years, so that power scrapers up to 6-yd capacity and carry-all scrapers up to 24-yd capacity are now used. If such equipment does not clean up well where the rock surface is irregular, the slackline and drag scrapers may be used where the dumping area is at the side of the quarry.

Transportation—Tractors with trailers are suitable for the shorter hauls of wastes to the dump, trucks for the short and intermediate hauls, locomotives with cars for the intermediate and long hauls. For conditions

of deep overburden and long haul, locomotives with contractor-type side-dump cars give the lowest costs as a general rule. Diesel power is fast replacing steam locomotives for this purpose. If dragline equipment is used, the number of track changes at the stripping site is about one half that required for shovel equipment, for the dragline has a reach of about twice that of its equivalent in the dipper type of shovel. Track-shifting machines are obtainable in standard and narrow gauge for use on the dump. When trucks are used, it is well to provide a tractor with scraper, or bulldozer, for trimming the dump and maintaining the road.

Belt conveyors are used occasionally to convey the waste to the dump. The size of the conveyor is dependent on the size of the lumps or boulders to be handled, so that it is applicable to larger operations or those handling friable soil free of large boulders.

Where the area to be stripped is narrow and the wastes can be disposed of at the sides, overcasting with dragline is most economical. This operation is one of throwing the excavated material from the bucket as far to one side as can be reached without the use of transportation equipment. If the pit is too broad to do this in one operation, overcasting the same material several times to reach the disposal area is often warranted by the elimination of any transportation cost. This applies only to handling shallow overburden, for where the overburden is deep the pile may become too high for the dragline to handle. Overcasting is also practicable in quarries having thin horizontal beds, where the wastes may be disposed of in the area that has been quarried out. This is the method used extensively in the strip coal mines. A portable belt conveyor carried along with shovel or dragline will extend the latitude of operations but is limited by conditions noted in the preceding paragraph.

QUARRYING

Quarries are of two different types, the pit quarry and the bank quarry. The pit quarry is one in which the stone is extracted from below the general level of the surrounding country, and, as a rule, the stone is elevated to the crushing and treatment plant on the surface. Some operations in limestone and granite are of this type. The bank quarry is one in which the stone is taken mostly from above the level of the adjacent country. The rock is shot down to about the level of the crusher and no hoisting is required. Quarries of this type are generally self-draining and as a rule have no pumping problems.

In flat-bedded deposits, the quarry layout can generally be made to suit the plant location, highways, railroads, or other topographical features. The layout is more involved, however, where the strata are pitching and narrow. The hoist or point of attack should preferably be at the midpoint, along the strike, to reduce the average haul. The quarry face

should be across the strata, at right angles to the strike for better breakage in blasting. Blasting a face lengthwise of the strata will cause a slippage on the bedding planes, create an overhang on one side and heavy toe on the other. The slope of the bench should be upward at about 0.5 to 1.0 pct, to drain water from the loading place and back to a central sump. Also, this slope tends to equalize the hauling efforts by favoring the loads.

High faces are common in bank quarries because of the desirability of getting the blasted stone down to the crusher level. In pit quarries the height of face for each bench is governed by the size of the shovel, character of rock, amount of water to be pumped, and the necessity for providing more working points to increase production. In seamy rock that does not break up well in the primary blast, the face should be lowered, for where large blocks remain in the blasted material above the reach of the shovel, undercutting of the pile is necessary to bring them down and delays result in waiting for blockholing and blasting after the blocks are exposed.

Pumping costs can be reduced considerably in pit quarries by developing the working levels at short intervals; for example, instead of developing a level with a high face, if the same depth were developed in two stages the pumping head would be reduced by half the height of the high face of the first plan for the period of time required to quarry the stone lying above the first stage of the second plan.

Drilling and Blasting

The distance from the toe of the face to the line of drill holes for primary blasting is called the "burden" and the distance between the holes in the line is called the "spacing." Although suggested burdens and spacings are given in handbooks on the use of explosives, generally the drilling and blasting practice in any quarry must be developed by trying various burdens and spacings with the explosive likely to be adapted to the character of the rock, until a combination is found that gives the results sought.

There is a difference of opinion on the best size and spacing of drill holes. One group maintains that solid rock is a good conductor of the shattering force of an explosion and claims that the explosive should be concentrated at fewer points to give greater disruptive effect. This leads to the use of holes of large diameter with greater burden and spacing. Another group believes in a greater distribution of the total explosive charge by the use of smaller holes with closer spacing and lighter burden. The operator must study the characteristics of the formation of his quarry and decide which of these systems is likely to be preferable.

In the softer rocks associated with open or clay-filled seams, too much explosive at one point will tend to pulverize the stone adjacent

to the drill hole and the shattering force will be cushioned by the clay or air space, leaving many large blocks unbroken. The larger holes with wider spacing are more applicable to the hard, dense rocks, such as trap.

As the purpose of drilling is to provide space within the body of rock for sufficient explosive, a comparison of drilling costs must be based upon the volume of the hole that is proportional to the square of the diameter. Chambering (springing) is often resorted to in hammer-drill holes to enlarge them for primary blasting, particularly when they are horizontal, or nearly so. It is seldom practiced in well-drill holes.

For drilling, the hammer drill may serve well in thin strata of limestone worked in one bench, or worked upon several benches separated by well-defined parting planes. In these places, the rock surface can be more easily cleaned; but when there is broken rock on the benches for some depth, it must be cleaned off to start the holes or else casing must be used through the broken material, to prevent it from falling into the hole. The expense of either is likely to offset the lower cost of this type of drilling. This broken rock results from overdrilling the holes of the bench above, which is necessary to break the toe where natural parting planes do not exist at the bench level.

The hammer drill using hollow drill steel has had great usefulness in quarrying. It is built in sizes large enough to bottom a hole 2 in. in diameter at a depth of 35 ft. The larger sizes of hammer drills for primary drilling are preferably mounted on wagons for ease in moving, setting up, and handling the long drill rods. Hammer drills for block-holing are built in sizes as light as 20 lb, although a 40-lb machine is about the lightest suitable for quarry work.

Detachable bits are now in common use. They effect a saving in underground mining where the handling of drill steel between sharpening shop and the working face is always a problem and an expense. They are particularly well suited to the small quarry, where getting forged bits properly dressed and tempered may be difficult. There is also less investment in steel than when carrying the larger quantity of different lengths necessary with forged bits.

The well drill is most commonly used in drilling for primary blasts. The standard machine employs a $5\frac{5}{8}$ -in. bit for the tougher rocks and where greater spacing is practiced 8-in. holes are common and even larger holes are used. Drilling is carried 2 to 5 ft below the bench level, depending upon the burden and character of the rock, to avoid unbroken toes. Drilling too deep is to be avoided, for it makes it difficult for the shovel to maintain a level floor and requires more casing in drilling the bench beneath. All holes should be drilled accurately to depth. If the surface is irregular, accurate determination of the depth can be made by the drill operator with a hand level, sighting upon an established gauge. A log of the holes should be kept for reference in

loading the shot. Explosive placed in clay seams is wasted and such waste may be avoided by splitting the charge, so that the explosive is placed in solid rock and stemming placed in clay or open seams.

Data on the costs of well drilling seem to be rather scarce in the quarrying literature. Well-drilling costs were discussed at the Operating Session of the Thirtieth Annual Convention of the National Crushed Stone Association and Table 8 shows a survey of costs in five different types of rock and different sizes of holes. In the *Proceedings* of that meeting⁷⁰ there is a statement that the 9 $\frac{3}{4}$ -in. drills are producing more footage than the 6-in. drills and Table 8 is discussed as follows:

TABLE 8—Survey of Well-drilling Costs for 1946

Quarry	Stone	L. A. Rattler, Pct	Wt per Cu Ft Stone (Solid), Lb	Wt Drill Tools, Lb	Size of Hole, In.	Avg Ft Drilled per Hr per Machine	Cost per Ft	Cost of Drilling per Ton Stone	Tons per Ft of Hole	Tons per Lb of Explosive	Ft per Bit
A	Limestone...	25	176	2,200	9 $\frac{1}{4}$	3.32	\$1.62	\$0.0312	51.3	4.83	92.4
B	Limestone...		163	1,950	6 $\frac{3}{8}$	2.30			50.2	3.07	55.0
C	Limestone...	Hard	168	1,900	8	2.40	1.00	0.0531	26.0	3.15	
D	Limestone...	29	160	1,842	8	4.00	0.77	0.039	30.0	3.35	
E	Limestone...	21	170	1,600	6	2.80	1.08	0.069	15.5	3.00	
F	Dolomite...	23	177	1,500	6 $\frac{1}{2}$	1.70	1.43	0.0279	51.3	4.92	27.0
G	Dolomite...	19	167	1,200	6	2.69	1.23	0.069	17.9	2.60	10.0
H	Dolomite...	22	176	2,200	9 $\frac{1}{4}$	2.56	2.33	0.0489	52.2	5.91	19.8
I	Dolomite...	25	168	1,800	6	6.00	0.53	0.037	14.4	3.00	
J	Dolomite...		172	1,330	6	2.40	0.99	0.04	24.5	4.00	
K	Trap.....		180	2,500	9	2.00		0.09	65.0	5.00	
L	Trap.....	22	176	4,000	9 $\frac{1}{4}$	3.04	2.34	0.0382	61.3	6.37	8.1
M	Granite.....			2,000	6 $\frac{3}{8}$	1.02	2.25	0.05	45.0	5.00	6.3
N	Granite.....	45	165	1,800	6 $\frac{3}{8}$	0.82	2.57	0.055	46.7	3.53	6.0
O	Granite.....	43	167	1,700	6	1.43	2.36	0.085	28.0	3.72	2.0
P	Diorite.....	17	183	2,200	6 $\frac{3}{8}$	0.80	3.55	0.0478	74.3	7.50	2.4

"Powder costs on the primary shooting can be arrived at from this table fairly closely. There is, in the next to the last column, tons per pound of powder used by primary shots. These vary from 2.6 tons per pound to 7.5, which is quite a variation. The 2.6 on a dolomite was for a 6-in. hole; the 7.5 is a diorite rock with 6 $\frac{3}{8}$ -in. hole. The 9-in. holes, on the use of powder per ton of stone broken down, seem to be reasonably consistent, around 5 to 6 tons per pound. That, I believe, just glancing at the table, is a better yield of stone than the smaller diameter holes which look as though they would average somewhere around 4. When you compare the large-diameter hole for overall results, there are other factors, of course, than the dynamite costs. You will immediately bring in the question of what breakage will occur, whether

that breakage is better or poorer. Our own experience is that a little more money spent on primary drilling can quite often yield a great saving on the floor of the quarry in shovel capacity."

Multiple rows are often used, sometimes getting better fragmentation, but the particular advantage results from the reduction of the number of blasts with attendant cessation of operations near the face while the holes are being charged. Drilling costs are increased, for it is general practice to reduce the burden on the second and subsequent row of holes. Usually, holes are staggered from row to row.

Another very interesting development in connection with drilling is that of an air-operated drill, which hits 200 to 220 blows per minute, as compared with about 60 blows per minute in the gravity-fed type of churn drill. This is a percussion type of drill, which experimentally is being used on 6-in. holes. It is claimed that the drill performs a chipping rather than a crushing operation. The cuttings are swept out of the bottom of the hole by compressed air. Apparently, with this type of drill, instead of turning the bit 180° at one time, striking it several times in a spot, and then turning it again, the rotation of the bit is controlled so that each blow of the bit on the face of the hole is properly burdened. In other words, a chip is taken off at a time as the drill is gradually rotated in the bottom of the hole. The hole is continuously cleaned by air forced to the face of the bit and the chips are blown out of the hole by the exhaust air. This is a recent development and promises to speed up the drilling of well holes to a very considerable degree.

"Upper" and "blanket" shooting are terms applied to making a blast before the preceding one is entirely cleaned up. A bank of loose stone prevents scattering of the rock out of the quarry floor and confines it to afford better loading conditions for the shovel, reduces the labor of cleaning up the floor, and reduces trackwork where this type of hauling is used. Better fragmentation may result, although this is questionable.

"Snake-hole" blasting requires that the drilling be done after the shovel has cleaned out the preceding shot, so that it is applicable to long faces where time is afforded to accomplish the drilling before the shovel returns on the next cut. A modification of this method for use on higher faces is to shoot the snake holes and then set the drill upon the pile of blasted rock to drill the unbroken bank above.

Tunnel blasting (known also as gopher-hole or coyote-hole blasting) may be practiced upon high faces where the structure of the rock is favorable. Small tunnels are driven into the face at the floor level and laterals in both directions from the end of the tunnel parallel with the face. The explosive placed in the laterals breaks out a wedge-shaped section at the base; the part of the rock above this is lifted slightly, then falls of its own weight. The structure of the rock must be such as to

give good fragmentation in this fall. The columnar structure found in basalt is very favorable for good fragmentation. Tunnel blasting is not applicable to flat-bedded rocks, where an overhang would remain, nor to badly faulted rock. Sometimes well-drill holes are put down part way from the top to be shot simultaneously with the tunnel blast, aiding in fragmentation and also helping to control the line of back breakage and prevent overhang.

Delayed-action Blasting

A very interesting and useful development in the quarrying industry within the past several years has been that of delayed-action blasting. The following is quoted from a recent paper by Nelson Severinghaus:⁷⁷

"About the most interesting development in quarrying in recent years has been extensive experimentation with short-interval delays between adjacent holes in primary blasting. These delays are achieved by timing switches in conjunction with instantaneous caps or by delay caps. Some work was done years ago with electrical timing switches. Their use seems to have lapsed until recent years because of the hazard of misfires under some conditions. Revival of interest was brought about largely by a need in some places to reduce vibration and consequent damage claims. Some quarries with nearby houses have been limited to uneconomical single-hole shots, or to smaller holes. Seismograph records of ground movement, occasioned by shots, have shown that in some cases as many as eight holes may be shot with short delay intervals (0.015 to 0.040 sec) between them and cause no more vibration than that from one hole. This system of shooting, which materially reduced vibration, has also quite generally produced improved fragmentation, with consequent lowering of secondary breaking costs.

"One school of thought on delay shooting recommends initiation of the explosion by delay caps placed near the bottom of the borehole. Their contention is that improved fragmentation and better toe removal came from bottom detonation at the 'tight part' of the face.

"Another school contends that the advantage gained by bottom shooting is not worth the increased hazard of loading occasioned by placing electric caps in the bottoms of holes. Those holding this view achieve delay by time switch shooting of instantaneous E. B. caps on top of primacord lines extending down into each hole. In either case there is some danger of the explosion in delayed hole being partially or fully cut off by ground movement. This delay is greater in friable rocks, in cracked up faces, and in places where hole spacing is close. Best spacing and delay interval for each rock condition are matters to be determined by experimentation. Results of the many tests now being run should soon find their way into the trade literature."

There have been some very interesting discussions of delayed-action blasting at several conventions of the National Crushed Stone Association, from which it is quite apparent that to obtain successful results as far as fragmentation and diminution of vibration are concerned, each quarry condition must be given separate study and the method to be pursued as to delay interval, size and spacing of hole, kind of powder, etc., must be determined for that particular quarry. It has happened in several instances that, although complete success was not obtained on the first shot, very great improvement in both fragmentation and vibration were achieved after a little experimentation.

Ammonium dynamite, which derives its strength largely from ammonium nitrate, is used in quarry work more than any other type of explosive. Its freezing point is lower, it is safer to handle, and it is cheaper than straight nitroglycerin dynamite. Ammonium nitrate is soluble in water, therefore cannot be used in wet holes. Gelatin dynamite will resist water indefinitely and is used under water where the pressure is considerable. Ammonia gelatin is a recent development and is becoming popular for quarry use. It is similar to straight gelatin dynamite but a portion of the nitroglycerin is replaced by ammonium nitrate. It is water-resistant to a limited extent and can be used in wet holes if the water is not so deep as to subject the explosive to considerable pressure.

Various strengths of high explosives are used, 20 to 30 pct for block holing, 30 to 40 pct for shales and cement rock, 40 to 60 pct for limestones, and 60 to 75 pct for traps and granites. Often an explosive of greater strength is placed in the bottom of the deeper holes to give better breakage at the toe, where the burden is greatest.

Gelatin dynamite has the highest rate of detonation and is used for the tougher rocks. In limestone and softer rocks, less pulverizing action nearer the charge and more uniform fragmentation are secured by the use of lower velocities. Lower velocity is also secured with larger grain size of the ingredients of the explosive.

Black powder, nitrostarch, and liquid oxygen explosive (LOX) are also used in the quarrying industry; to a lesser extent, however, than the previously mentioned explosives.

During the primary blast, insufficient fragmentation may result in the formation of blocks of stone that are too large to be handled by the primary crusher. These must be broken down by some means, in order to be usable. The use of mud capping and of jackhammer drilling and blasting is very common, but jackhammer drilling has long been regarded as an undesirable type of work in the quarry and in recent years an old method of rock breaking has been revived; namely, the use of the drop ball. Highly mobile, single-operated crawler cranes are used for hoisting and dropping a heavy steel "ball" weighing about

7000 lb. Generally a $1\frac{1}{2}$ -yd crane, equipped with a 60-ft boom, has been found suitable. Such a rig will break a 30-ton rock of almost any toughness. It can also be used for knocking down dangerously high piles of stone and in scaling loose pieces from the quarry face. It has been reported that a drop ball manipulated by one crane can do the work of 6 to 10 men operating jackhammers. Its use is spreading very rapidly. There has been experimentation on the shape and weight of the ball, on replaceable striking faces, on the kind of hitch to be used in fastening the hoisting cable to the ball, and on the method of operation. A steel billet of hexagonal cross section makes a suitable weight or "ball." These matters are discussed in some of the literature on the subject. Much of it is covered by the reports of the operating men's sessions of the National Crushed Stone Association for the years 1946 and 1947.

Loading

Hand loading is rare but is still done where careful selection of the stone is necessary or in small operations at some distance from well-equipped plants. Naturally the cost of explosives becomes high in a hand-loading operation because of the necessity for blasting the stone to sizes small enough to be handled.

Power shovels are virtually indispensable in the average quarry, and even the smaller quarries use them because of the difficulty of securing hand-loaders. Shovels are now made with dippers of capacities from $\frac{3}{8}$ to 32 cu yd. The larger sizes are built more for stripping operation where overcasting is possible and a long reach is desirable. A shovel with capacity as great as that of the transportation system would seem adequate but too small a shovel is uneconomical, even though its capacity may be as high as the plant is designed for. The uneconomical feature of smaller shovels is their inability to handle the larger pieces of rock left in the primary blast. This causes delays and the expense in preparing the large blocks for the primary crusher. In loading stone that is well broken up in the primary blast—shale or cement rock—excessively large pieces offer no particular problem, but in many limestone quarries having seams of clay, the primary blast may not spread the stone down sufficiently upon the floor, and the shovel must pull it out of the bank. This is hard on the shovel frame and mechanism and the smaller shovels cannot perform this operation without entailing heavy expense for repairs. In hard digging, lower costs for repairs warrant the use of a shovel with a dipper one size smaller than that for which it is designed. The popular sizes of shovels are from $1\frac{1}{2}$ to 4 cu yd for larger quarries and $\frac{3}{4}$ to $1\frac{1}{4}$ yd for quarries of 500 to 800 tons per day capacity. Larger shovels are slower in action and the loading capacity is not in proportion to the size of the dipper.

Electric shovels have become predominant in the larger quarries

while diesel shovels are largely used in the smaller units. Air power has been used for shovels in underground work, although it has been largely replaced by electricity. Steam still holds high favor because of its flexible power characteristics and its digging ability in tough work. However, because of boiler troubles and expense from hard water, necessity for service and supplying coal and water, and extra labor for firemen in the use of steam, the use of electric, gasoline and diesel shovels has been increasing.

Bulldozers have taken over the work of collecting scattered rock following shots, a job that formerly was done by hand or by "sweeping" with shovel dippers. Bulldozers are regarded now as an almost indispensable tool in quarries of any size. They save valuable shovel time and improve quarry transportation conditions.

Haulage

Although haulage from the loading point to the crusher was carried on formerly in large quarries by the use of either standard-gauge or narrow-gauge railroads, and is still so carried on, nonetheless there is a decided trend in the ordinary quarry toward the use of motor-truck haul. The motor units used are either truck or tractor-trailer units. Most of the newer trucks are diesel-powered because of the greater fuel economy. No doubt each quarry must be studied individually to determine the best type of motor unit for its particular condition. In one large plant, light tractor hauling units are used, either Ford or Chevrolet, handling trailers of 12 to 24 tons capacity. Such light tractors handle these heavy loads on relatively level grades and are drawn up heavy grades by the use of a powered cable, to the end of which is attached a Barney car, which returns the cable to the bottom of the grade for the next load. This system has been used successfully in a number of quarries. It is believed, however, that the haulage units are gradually becoming larger, so that one driver may handle more tonnage. These larger units are more rugged and lose less time for repairs.

If the tonnage capacity becomes so large that the dumping of one body tends to choke the crusher or overflow a feeder, dual bodies mounted on a single chassis have sometimes been adopted. Side-dumping bodies, which avoid backing up at the dumping point, are preferred in the more permanent installations. Rear-dump bodies, on the other hand, are common in portable and semiportable plants. The use of feeders ahead of the primary jaw crusher is becoming very common. It is said that in larger installations they increase the crusher capacity by a minimum of 20 to 30 pct. The use of vibrating pan feeders ahead of the primary crusher is finding favor, as they regulate the feed and also tilt the large pieces of stone so as to prevent clogging in the crusher. Delay in the primary crusher due to "hang-ups" is said to slow down

production by as much as 9 pct. There is a tendency toward placing the primary crusher in the quarry pit. Crushed stone from the primary crusher is transported to the plant by means of a belt conveyor, a bucket elevator, or a skip. Where motor trucks are used for hauling, it is very desirable to keep the roadway clean of stone, for thereby a great saving is effected in tire wear.

Derricks and cableways are used for hoisting stone boxes out of deep pits. In at least one recent installation, such devices have been replaced by belt conveyors from the quarry floor to the upper level.

CRUSHING

Primary Crushing

Jaw crushers of the Blake type and the gyratory crusher are used for primary breaking. Roll jaw crushers (single roll and baffle plate) and hammer mills are sometimes used as primary crushers where the rock is of the soft and friable type. Other heavy-impact crushers have been used successfully, particularly in the softer type of stone. Crushers with frames of welded steel plate are gradually supplanting those of cast iron and cast steel, with consequent lower weight and greater strength. At least one manufacturer has used the electric-welded type of fabrication on the gyratory crusher.

Jaw crushers are built with openings up to 66 by 86 in. and gyratories up to 84 in. The size of the opening should be more than ample to pass pieces that can be carried by the dipper of the shovel. Often pieces that are smaller than the opening of the crusher may arch against each other and bridge across the mouth of the crusher; a pan feeder reduces the chances of bridging, but when such bridging does occur, the feed may be stopped to loosen the jam without having to dig out a lot of rock that otherwise would be piled above the crusher. Use of a feeder permits the use of a slightly smaller primary crusher; also, it gives a steady flow of material through the plant and reduces the fines through a reduction in choke feeding.

For the harder rocks, the reduction in the primary crusher should be less than 6 to 1. Greater reduction than this tends to move the stone upward against the fixed jaw or concave and will greatly increase the stresses in the machine. With certain types of rock that tend to break in a slabby shape, some pieces of the product may be several times the size of the discharge opening in one direction. The use of corrugated jaw plates in the jaw crusher tends to reduce the slabby pieces and the gyratory crusher is said to give a product more cubical in shape because of the curved crushing faces.

A feeder under the primary crusher saves the conveying belt from wear and cutting by falling stone and is very necessary where clay

is present in the stone, because the lubricating effect of the clay tends to give the stone high velocity when sliding down a fixed plate chute. If a feeder is not installed, a grizzly chute that allows the fines to drop through to the belt first, to form a pad to receive the larger pieces, is very desirable. The use of a surge pile following the primary crusher is rapidly coming into use, particularly where the primary crusher is in the quarry and a belt conveyor carries the stone up and discharges over the surge pile for withdrawal to the plant by tunnel conveyor. This is an insurance against breakdowns in the quarry and unfavorable weather conditions for getting out the stone. It is a means of keeping the crushing and screening plant uniformly loaded at a high level of capacity.

Secondary Crushing

The demand for more and more fine stone for use in highway maintenance work and for other purposes has been growing. In many plants the bulk of the production must be less than one inch in size. This trend has some effect on the type of secondary crushers used, and cone crushers and high-speed flat-angle gyratories are very popular in the larger plants for the production of increasing quantities of smaller sizes. For the less abrasive types of rock, hammer mills and other impact types also are used. Special impact crushers of the squirrel-cage type have been used to reduce the quantity of soft pieces and at the same time to improve the shape of particle, thus permitting the stone to qualify under the highway specifications for abrasion loss.

Jaw and gyratory crushers are now on the market permitting a double reduction in a single pass, fines from the first reduction being by-passed. A better particle shape and fewer fines are said to be thereby produced.

Fine Crushing and Pulverizing

For fine crushing, many different types of machines are used, many employing the gyratory principle but having variations in the shape of the crushing surfaces. In the gyratory crusher, as the space between the crushing surfaces becomes smaller as the material passes through the crusher, the circumference must become larger to provide sufficient space to prevent blocking of the stone in its natural flow. This principle has led to the design of bellheads, spherical heads and flattened cones. Double-roll crushers having large capacity and relatively low headroom are used for fine reduction, and even for the production of stone sand. Rod mills are coming into favor for fine crushing such as is required for stone sand, where particle shape is an important factor.

The selection of machines for fine grinding must be based on the characteristics of the stone to be ground and the fineness specifications to be met in the finished product.

Hammer mills are used on the less abrasive rocks having a low percentage of silica, for the production of smaller sizes where the proportion of fines needs to be kept low. The swing-hammer mill of the small size can be considered as a fine grinder and is so used for the production of the coarser meals, such as agricultural limestone and the coarser grades of poultry grit, where the tonnage is small and simplicity of operation is important. It cannot be used on the harder rocks such as granite and trap.

The types of pulverizers most generally used are the rod mill, ball mill and tube mill (ball-bearing type) and the roller mill (edge runner).

When extreme fineness is required, closed-circuit grinding is practiced. The dust formed is of a rather uniform size, but this may or may not be desirable, depending upon the use for which the finely ground material is intended.

Rock dust such as is used for mine dusting and asphalt filler is usually ground dry; coarser products, such as crushed sand and glass sand, are frequently ground wet. When the moisture content of the feed is not too high, drying may be accomplished in the grinding mill by heating the air used in sweeping the mill. Of recent years, fine grinding to produce agricultural limestone has become a very important part of the limestone business, and many commercial stone operators have converted their plants to use a very high percentage of their capacity for pulverizing agricultural limestone. A number of plants have come into existence purely for the purpose of making agricultural limestone, but the danger of having only a single market was soon realized when production subsidized by the Federal Government greatly reduced the private operator's participation in the soil improvement program. Some of these plants are now casting about for commercial markets for their stone in the construction field.

Elevating and Conveying

For conveying material within the plant and for elevating where space permits, the belt conveyor is very satisfactory. The maximum slope permissible is about 18° (about 33.5 pct) but this may be exceeded if loading with fine or graded material is continuous. It is important that care be used in the design of the method for feeding the belt, so as to drop the material lightly and in the direction of the belt travel. Proper loading of the belt will permit higher speeds and will allow the use of the narrower belts.

The bucket elevator is commonly used in stone plants, especially where ground space does not permit the use of belt conveyors. Where a steeply inclined conveyor is necessary, the automatically controlled skip hoist is sometimes used instead of bucket conveyors. The first cost of the skip is high, its operation intermittent, and it requires a bin and feeder to give steady flow of material through the plant.

Pan conveyors are used for conveying short distances and are particularly suited for lump material for feeders. Numerous other types of conveyors, such as the drag, screw, vibrating and pneumatic feeders, are used, but these are not so frequently seen in crushed-stone plants.

Screening

Revolving and trommel screens, which were so universally used in crushed-stone plants some years ago, have been almost entirely superseded by vibrating screens, although they are still used to some extent as scalping screens for larger sizes, preliminary to crushing and screening operations, or as an integral part of revolving scrubbers. They do not serve well for screen sizes of less than $\frac{1}{2}$ -in., particularly when the material is damp. It is preferable to have the holes in the barrel not smaller than 1 in., obtaining the required smaller sizes through jackets. The vibrating screen, which was used originally for very fine screening, is now used for all sizes, even in one instance for the production of riprap.

The size of the material to be screened dictates the type, magnitude and frequency of vibration. The tendency is toward flatter screen surfaces, for more thorough and more accurate sizing. Horizontal vibrating screens are common. Vibration is imparted to the screen surface generally by mechanical vibration of the frame, but also by direct vibration of the screen cloth. The vibration effect is produced by eccentrics, by cams and by electric solenoids. Vibrating screens are made in single, double, triple, and quadruple decks. In the triple and quadruple deck types, the capacity factors on the lower decks must be corrected because the feed drops on the screen cloth at different distances from the end of the screen. For making a single separation into two sizes of material running through a comparatively long range in size, it is advisable to use double-deck screens, the upper deck with heavier cloth or plate to protect the finer cloth on the lower deck from wear by the larger particles. For efficient screening to specification size, it is necessary that a sufficiently large screen area be provided to permit every particle to come into contact with the screen cloth at some stage in its travel over the screen.

For scalping where accurate sizing is not required, bar grizzlies are used. To reduce binding, the bars should be rolled with a taper. Scrap steel rail with the lower flange cut off makes an ideal grizzly bar and gives very little trouble from binding. For very abrasive stone, manganese-steel bars are desirable.

A live roll grizzly is highly satisfactory for screening larger sizes. It consists of a series of horizontal rolls laid on a slope, each roll grooved to give the screening size desired, allowing the oversize to fall through. This roll is turned at a slightly greater speed than the preceding one,

to minimize the crushing action between rolls. It has large capacity per unit of floor space occupied.

Washing

In former years, crushed stone was seldom washed, but washing is becoming more generally practiced. A common method of washing is to use water jets upon the stone during its passage over the screens. This method is satisfactory if the stone is merely coated with dust, which is readily separated from the stone. A simple means of avoiding trouble from clogging of the fine holes used in some types of sprays is to employ a relatively large jet with a round hole and spray the stream of water against a curved plate, thus giving a fishtail type of spray.

Scrubbers are not uncommon; they consist of a cylindrical or conical shell fitted inside with lifting plates to agitate the material and carry it forward. Chains sometimes are suspended inside the shell to increase the rubbing action, particularly in treating smaller sizes. Restricted openings at the ends keep a certain level of water in the shell; the flow of wash water may be counter to that of the stone or may be discharged with the stone, to be later separated on the screen. A dewatering and sizing screen may be integral with this scrubber or may be a separate device. The scrubber described will remove a coating of clay or soil and will break up the more friable material.

When the stone is mixed with exceedingly tough clay, a greater churning and grinding action is necessary. For this type of scrubbing, a log washer is quite commonly employed. It consists essentially of two parallel shafts upon which are mounted a series of paddles. These shafts are sloped at an angle of 5° to 10° . The material is fed into a trough near the lower end and the stone is moved up the incline and discharged out the front end by the propeller action of the paddles. The lifting and churning actions of the blades cut and reduce the clay balls and the action of the stone working one piece against another further grinds and scours the clay, so that clay and finer particles of stone dust float off in suspension in a counter current of water. The speed of the log washer is from about 16 to 25 rpm. Other types of scrubbers and washers have been developed using the principle of the ball mill, in which the stone and clay balls grind against one another. Still other devices employ the combined principle of the log washer and the scrubber.

Stock Piles

Storage bins usually are sufficient for only one day's run but in some places large silos have been used. Ground storage is quite commonly practiced to provide for variations in demand for different sizes of stone. In some of the newer plants, circular stock piles are built up surrounding towers supporting the secondary screens for each particular size. Recovery from these stock piles is made from an underground

tunnel carrying a belt conveyor, leading to a central loading point. Several sizes may be combined as desired by regulating the feed of each size to the recovery belt. When this belt system is not used, recovery from stock piles may be made by small shovel, bucket loader, or drag scraper.

The building up of a stock pile in layers is desirable since it minimizes segregation. Large stock piles usually are built up by elevating conveyors with trippers to discharge the belt at any desired point. Traveling cranes, excavators equipped with long booms, and clamshell buckets or drag scrapers may be used to clean up the material that lies beyond the natural slope of the tunnel gate leading to the underground recovery system. In the radial storage system, the stone is dumped from a fixed point and chuted to any of a number of compartments radiating from the central point. Shipment loading is from a single point beneath. A circular track about the piles may carry a traveling crane or a traveling tower for a drag scraper to serve for moving the material from the live-load space to dead storage and reclaiming it again when required.

To reduce the breakage of stone falling to bins or storage piles, a lowering ladder is sometimes used. This consists of a vertical chute filled with baffles at short intervals, which break the fall of the stone into many short cascades. A screen is sometimes provided at the end of a reclaiming belt to remove any fines produced in stock-piling.

UNDERGROUND MINING

Although crushed stone usually is produced in the open-pit quarry, production by mining has greatly increased of recent years. A number of conditions necessitate use of mining operations, such as excessive overburden and the location of strata having favorable physical or chemical characteristics. Advantages of mining are the production of a cleaner stone, protection from inclement weather, with a resulting steadier production, and, with some mining methods, the ability to use stopes for the storage of broken stone.

As the product, crushed stone, has low value, mining methods using a minimum of expensive timbering are employed. Frequently the underground operations are started by driving tunnels from the open pit into flat-lying or inclined strata, when the overburden becomes too heavy for economical removal. This develops into tunnel mining or breast stoping. The tunnel is fanned out to provide a working face (breast) and pillars of rock are left at irregular intervals to support the roof. The size and spacing of the pillars is dependent upon the strength of the rock in the pillars, the pressure of the ground, and the character of the roof. Breast stoping consists of breaking the stone from the vertical face for the entire height in one operation. It is applicable to strata not more than 10 to 12 ft thick and those lying flat or nearly so.

The room-and-pillar system of mining differs from breast stoping only in the manner of developing along precise mathematical lines, leaving regular pillars evenly spaced. This system may also be used in slightly inclined strata, driving the rooms level along the strike of the deposit. In flat strata, thicker than 10 to 12 ft, a combination of the breast stope with underhand or back stope, or both of these, may be used. Here entry is gained by breast stoping and from this entry the bottom or the back is drilled and broken. The back may be drilled from the top of the broken rock, as in the shrinkage-stope system. The glory-hole (milling) and the shrinkage-stope systems are used for thick deposits and steeply inclined strata.

In the shrinkage-stope system, 60 to 70 pct of the broken stone is left in the stope and cannot be drawn until the stope has been entirely completed, so development must proceed well in advance of shipping requirements. This entails considerable development expense but it provides a large reserve of broken stone to meet irregularities in demand. Many variations of these systems are used as the case may require..

PORTABLE PLANTS

Highly efficient portable plants, mounted on pneumatic-tired wheels, are now available. Such plants are used as a rule in locations where freight rates on stone produced at permanently established plants make its cost prohibitive. One advantage of the portable or semiportable plant, in addition to saving transportation cost on stone, is that it can be moved from point to point of the deposit, with the result that selective quarrying may be employed. Disadvantages are high labor costs and higher cost of drilling and explosives because of the smaller crushers used. There is also frequently a waste in sizes that cannot be used on a specific project. Delays in the construction work may be caused by breakdowns of the stone plant unless large stock piles are maintained. These points are too frequently overlooked by the contractor when planning the installment of his own plant. The commercial producer can furnish the exact quantity of sizes required, with no waste to the contractor, and will deliver at the peak demand to keep the work progressing at maximum efficiency. Contractors have used several portable plants for a single job in order to obtain a high production rate. Sometimes insufficient investigative work has been done on the quality of the material before a portable plant was set up, with the result that the material has later proved to be of poor quality. Many commercial producers, in order to meet competition, have provided themselves with portable plants which they are prepared to operate for the contractor. With this arrangement, a commercial producer can decide whether it would pay to ship from the portable plant or from his commercial operation.

Furthermore, he can take care of peak loads from his commercial plant whenever necessary.

PRODUCTION OF STONE SAND

Stone sand for use as a fine aggregate in concrete seems to be gaining in favor. Almost invariably when stone is the coarse aggregate for use in large dams, the fines are utilized for the production of stone-sand fine aggregate. It seems to be desirable that there be a minimum of flat and elongated pieces in stone sand and where the stone is not abrasive, hammer mills or other impact types of crushers are used very successfully. One very successful type of crusher for use in production of stone sand is the rod mill, using wet-grinding methods and employing a feed of not over one inch in size. In many cases the screenings resulting from the primary crusher are purposely omitted from the stone sand because of the possibility that they may retain more dirt than the secondary screenings, and also because they are more likely to be slivery in shape. Sometimes the sand is made up of screenings resulting from the gyratory or cone type of secondary crusher, from rod mills and rolls, all combined. Excessive dust passing through the 100-mesh sieve is removed sometimes by the dry process but more commonly by the wet process. Various types of classifiers are employed, depending in general upon separation of particle sizes by the carrying capacity of water flowing at different velocities. Different ideas among engineers have developed with regard to what constitutes a desirable gradation for stone sand. The following is given as an example of what would seem to be an excellent gradation, though one not easily produced:

SIZE	PCT	SIZE	PCT
$\frac{3}{8}$ -in. to No. 4 mesh	1	Mesh:	
Mesh:		30-50	22
4-8	12	50-100	18
8-16	16	-100	6
16-30	25		

Sand having such a gradation should give workable concrete even though the particles may not all be cubical in shape. If an air-entraining agent is used, enough fines are present in this gradation to make the sand react as it should for the production of air in the concrete. Stone sand can be produced commercially only as a by-product in the production of numerous other sizes of stone, and, in general, the expense of its production is too great to permit stone sand to compete with a suitable natural sand that lies in the same production area.

COST AND CAPITAL INVESTMENT

Labor and other costs have been varying so rapidly in the past few years that no attempt can be made to give any idea of costs as they are

at the present time. The figures in Table 9 for the capital investment per annual ton of production at crushed-stone plants were published by the Bureau of Mines in 1931. These are depleted values representing the actual replacement values of the land, buildings and equipment, and new costs would be somewhat higher. The figures do not include financing, promotional, or additional operating expenses. For all the quarries reported, the investment in land and mineral rights amounts to 19¢ and the plant equipment to \$1.06 per annual ton capacity.

TABLE 9—*Capital Investment per Annual Ton of Production at Crushed-stone Plants*^a

PLANTS	INVESTMENT PER TON
Average of 16 limestone plants each producing less than 100,000 tons per year	\$2.12
Average of 10 limestone plants each producing between 100,000 and 250,000 tons per year	1.28
Average of 9 limestone plants each producing between 250,000 and 500,000 tons per year	1.48
Average of 5 limestone plants each producing between 500,000 and 1,000,000 tons per year	1.21
Average of 8 limestone plants each producing over 1,000,000 tons per year	1.14
Average of 4 granite plants	1.20
Average of 12 trap-rock plants	1.68
Average of all plants listed above	1.25

^a From Oliver Bowles.⁵

MARKETING

As mentioned before, crushed stone, being a low-cost product, is generally marketed locally. Seldom does the market distance exceed 50 to 100 miles. Generally competition is so keen that prices do not greatly exceed the costs. Much of the crushed stone goes into highway construction and for this purpose stone has been in great demand for the past several years. Generally the specifications of the state highway departments govern work of this nature and the gradation requirements are rather definite.

Acceptance is generally at the point of destination rather than at the quarry. This fact leads to difficulty at times, because in handling stone from the stock pile to the car, and from the car to the truck, segregation may occur, and although the stone may have been sized properly at the plant, samples taken at point of destination may show lack of compliance with the size requirements. The necessity for care in loading cars and trucks to prevent segregation becomes all the more apparent.

Naturally, the demand for crushed stone is greatest during times of high construction activity, therefore stone production is of a sea-

sonal nature. Very little is shipped during the winter months except in the southern and Pacific states. Maintenance activities on the highways are intense during the spring of the year to repair the deteriorating effects of water and frost and of spring and winter traffic. Later in the spring, surface-treatment programs are in effect to bring the roads into a good state of repair before the heavy summer traffic commences. Consequently, early in the construction season small sizes are in great demand; larger sizes, for concrete and more permanent types of construction, are required later in the season as a rule, after grading of the subgrade has been completed and in the rush to complete concreting before freezing weather occurs.

Some products—for instance, fluxstone for use in blast furnaces—move more regularly and may be shipped greater distances than stone for commercial construction. Much of the stone for this purpose is shipped by water in the Great Lakes region. One ton of pig iron requires about 0.4 ton of limestone for the blast furnace and additional treatment in the manufacture of steel requires additional amounts in the open hearth and cupola. Recently, as a result of the necessity for intense production of pig iron during and after the war, the gradation of fluxstone has been materially altered. Formerly it was thought that for proper operation of the blast, large voids were necessary in the stone. Consequently, more or less one-size material—for instance, 2 or $2\frac{1}{2}$ to 4 in. or more—was used. Now, the minimum size has been reduced to roughly $\frac{3}{4}$ or 1 in. and apparently stone having a wide range in gradation gives entirely satisfactory results.

SUMMARY OF MODERN TRENDS

A partial summary of some of the modern trends in the crushed-stone industry is as follows:

1. The use of delayed-action blasting to produce better fragmentation and to greatly reduce the vibration due to blasting and thus minimize claims for alleged damage from blasting.
2. A revival of interest in using the drop ball for breaking oversize blocks, too large for use in the primary crusher.
3. A shift to diesel power, not only for the production of electric power for use in driving the plant but also for use as individual drives and for hauling equipment.
4. The trend to the use of surge piles, particularly where the primary crusher is in the quarry and a belt conveyor carries the stone up to the screening plant. Such a surge pile is insurance against breakdowns in the quarry and against unfavorable weather conditions and keeps the crushing and screening plant uniformly loaded at a high level at all times.

5. The growing shift to the use of motor trucks for quarry hauling, in some cases light tractors for hauling heavy trailers and in others heavy diesel-powered truck-hauling equipment.
6. Adoption of large-capacity earth-moving equipment for removing overburden; for instance, equipment used by contractors for road construction.
7. A tendency toward placing the primary crusher in the quarry, separated from the secondary crushing and screening plant.
8. The almost entire replacement of revolving screens by vibrating screens for nearly every purpose.
9. Gradual enlargement of well-drill holes, from 5 $\frac{5}{8}$ -in., formerly the standard, up to 9 in. The use of the wagon drill to a greater extent than hitherto, particularly for benches not exceeding 30 ft, and the increasing use of detachable drill bits for pneumatic machines and jackhammers.
10. The increasing use of pan feeders ahead of the primary crusher to regulate the rate of feed and to tilt the large pieces of stone so as to prevent jamming of the crusher.
11. The storage of stone, crushed and screened to specific sizes, in stock piles over belt conveyors working in tunnels under the stock piles, which provides flexibility in making stone of any desired gradation. This system promotes easy recovery from the stock pile.
12. A great increase in the production of agricultural limestone, which has required more fine-grinding equipment and redesigning of some plants for that purpose. Plants especially designed for agricultural limestone, however, are finding it expedient to enter the commercial stone market.
13. As a means of marketing their stone, some plants have entered into the ready-mix concrete business, and many of them are in the bituminous concrete field.

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CHAPTER 13

DIATOMITE

By ARTHUR B. CUMMINS* AND HENRY MULRYAN†

DIATOMITE is a hydrous or opaline form of silica, commonly known as diatomaceous earth, diatomaceous silica or kieselguhr. The term "infusorial earth" has lost its original meaning and today is incorrect in view of the distinctions between diatoms and infusoria. Various locality and variety names are obsolete but some retain local significance. Moler and Celite are trade names that have become associated with diatomite products from certain deposits in Denmark and near Lompoc, California.

COMPOSITION

Diatomite is essentially silica with some combined water (2 to 10 pct). Frequently it contains organic matter (from traces up to over 30 pct) and varying amounts of inorganic impurities such as sand, cryptocrystalline silica, clay, volcanic ash, calcium carbonate, magnesia and soluble salts. In the natural or crude state, diatomite contains from 10 to 65 pct or more of free water. Table 1 gives analyses of several diatomites from deposits of different types.

PROPERTIES

Pure varieties, either massive or stratified, are friable and porous, of low apparent density, and somewhat chalklike in appearance. Varieties containing organic matter vary from sedimentary oozes to peatlike materials. Impure varieties may be more or less claylike, sandy, calcareous or cherty. Compacted types approach porcellanite and silicified shales.

COLOR—white, cream, gray, tan, brown, greenish to nearly black. **HARDNESS**—light-weight varieties appear 1 to 1.5 because of porosity, but microscopic particles are 4.5 to 6.5. **SPECIFIC GRAVITY**—1.9 to 2.35. **APPARENT DENSITY**—dry block form, 20 to 40 lb per cu ft; dry powder, 5 to 16 lb per cu ft. **CRYSTAL SYSTEM**—generally amorphous (isotropic by X-ray diffraction) but frequently showing faint cristobalite pattern.^{67,68,70} **MELTING POINT**—1400° to 1650°C. **STREAK**—white. **LUSTER**

* Research Center, Johns-Manville Corporation, Finderne, New Jersey.

† Executive Vice President and General Manager, Sierra Talc Clay Co., Los Angeles, California.

TABLE 1—*Chemical Analyses of Diatomaceous Earths from Different Localities, Moisture-free Basis*

Constituent	Lompoc, Calif.	Jalisco, Mexico	Monterey Co., Calif.	Los Angeles Co., Calif.	Maryland	Germany	Algeria	Nova Scotia
Silica (SiO ₂).....	89.70	84.33	83.20	75.62	79.55	68.30	71.99	92.78
Alumina (Al ₂ O ₃)..	3.72	3.05	5.15	5.75	8.18	1.57	3.00	2.63
Iron oxide (Fe ₂ O ₃).....	1.09	0.92	1.58	2.56	2.62	2.37	1.12	1.21
Titanium oxide (TiO ₂).....	0.10		0.20	0.20	0.70	0.11	0.13	
Lime (CaO).....	0.35	0.29	1.30	3.30	0.25	tr	8.15	0.66
Magnesia (MgO).....	0.65	0.78	1.41	1.50	1.30	0.18	2.30	0.29
Alkalies (as Na ₂ O).....	0.82	1.48	1.40	2.16	1.31	0.84	0.63	0.46
Ignition loss (combined water, CO ₂ and organic matter)...	3.70	8.37	5.95	8.22	5.80	26.50	12.68	2.22
SO ₃ and Cl.....		0.90						
Total.....	100.15	100.12	100.19	99.36	99.71	99.96	100.00	100.25

—dull to earthy. CLEAVAGE—none. FRACTURE—parallel with bedding planes, conchoidal or irregular. TRANSPARENCY—opaque. TENACITY—crumbly to brittle. SOLUBILITY—insoluble in acids (except hydrofluoric), soluble in strong alkalies. LIQUID ABSORPTION—1.5 to 4.0 times its weight of water. INDEX OF REFRACTION—1.42 to 1.48. THERMAL CONDUCTIVITY (Sil-O-Cel powder, 16 lb per cu ft density)—0.73 Btu per sq ft per hr per in. thickness per 1°F at 1000°F mean.

MICROSCOPIC APPEARANCE

All diatomites consist of the siliceous remains of diatoms, in whole or partly fractured condition (sometimes associated with minor amounts of sponge residues, radiolaria, silicoflagellae and other microscopic organisms, both plant and animal). There is a great variety in the types and conditions of diatom residues. Some 8000 different species of diatoms have been identified and the shape, size and structure of these vary enormously. Figs 1 and 2 show two types of diatomites from western United States; Fig 3 shows a fresh-water diatomite from South America and Fig 4 a German Kieselguhr.

ORIGIN AND MODE OF OCCURRENCE

Diatomite is of organic origin, consisting of the fossil remains of microscopic aquatic plants known as diatoms, of the order Bacillaria. These minute organisms are distributed widely in nature, growing wherever conditions of light, moisture and food supply are favorable. Each tiny plant is enclosed in a siliceous envelope and when the organism dies it sinks to the bottom of the water, where the organic mat-

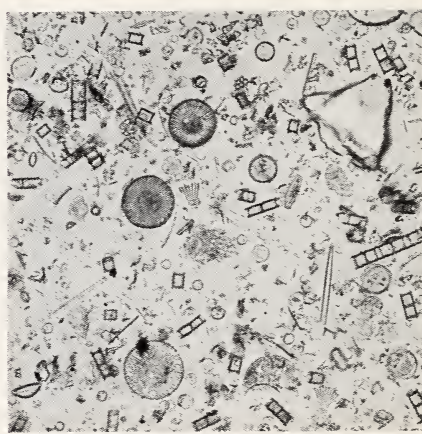
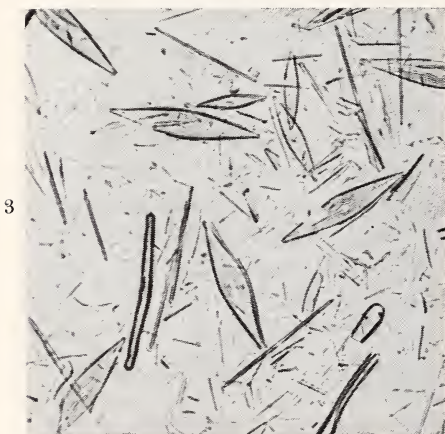
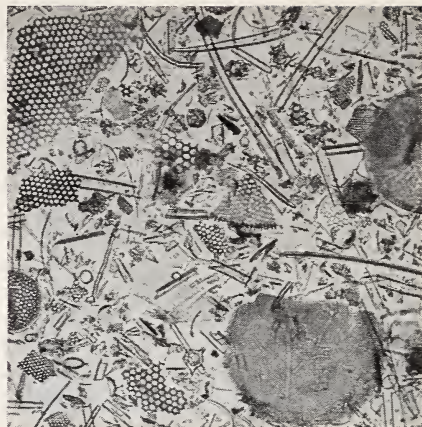


FIG 1—DIATOMITE FROM CARLIN, NEVADA. $\times 250$.

FIG 2—PROCESSED DIATOMACEOUS FILTER AID FROM LOMPOC, CALIFORNIA. $\times 250$.

Courtesy of Johns-Manville Corporation.

FIG 3—FRESH-WATER DIATOMITE, SOUTH AMERICA. $\times 250$.

FIG 4—GERMAN KIESELGUHR. $\times 250$.

ter is more or less decomposed, thus forming a deposit of the siliceous valves. The origin of diatomaceous peat deposits and the accumulation of diatomaceous residues has been considered by Conger.^{65,66}

Diatoms grew in great profusion during various geological periods, particularly the Miocene, and the most important economic workings today are in the fossil deposits of that period. Some deposits, however, are recent and others are in the course of formation. No large economic deposits are of earlier age than the Tertiary. Deposits are of both marine and fresh-water origin; in geologic age they range from the Cretaceous to the Recent.

The deposits near Lompoc, California, are of plankton marine

origin and belong to the Monterey series of the upper Miocene. The main deposit consists of 1400 ft or more of diatomaceous sediments, which have been folded into a series of synclines and anticlines. The area of the Celite deposit is some 4000 acres. Deposits in Los Angeles and Monterey Counties, California, are of different degrees of purity and of limited size. These are also of marine Tertiary origin. Some undeveloped deposits in lower California appear to occur in similar formations. Bramlette⁶⁴ has made an important contribution to knowledge of the Monterey formation of California and the origin of the diatomaceous rocks therein.

There are a considerable number of fresh-water deposits in the western states. All the known deposits of Oregon and Washington were laid down in fresh water in late Tertiary or Pleistocene times. They exist mainly as horizontal beds formed in prehistoric lakes. The numerous deposits of Nevada and some others of the western states (Arizona, Utah, Idaho, and New Mexico) also are of fresh-water origin. They occur as stratified basin-shaped beds, overlain and interlain with sedimentary and igneous formations.

Marine Tertiary deposits occur in Maryland and Virginia. The beds are intermixed and interstratified with sand and clay along the Potomac and Rappahanock Rivers and their tributaries. In New York, New Hampshire, the maritime provinces of Canada and Florida, there are recent deposits in ponds, peat bogs, marshes and small lakes.

The Algerian deposits are marine Miocene and occur in formations somewhat similar to those of the California coast regions. The French deposits are principally of fresh-water origin, having accumulated in Tertiary and Quaternary lake beds. Deposits in the Lausitz district, Germany, and those near Bilin, Czechoslovakia, are in an area of Tertiary basalt. The Lüneburger Heide deposits were formed in the last interglacial period and lie in water-soaked beds covered with soil and sand. The Danish deposits (late Tertiary) are of great thickness and are intimately mixed with clay. They are often exposed in sea cliffs. Japanese deposits on Hokkaido Island consist of compact massive beds (marine Tertiary) and contain clay, organic matter or volcanic ash. Other Japanese deposits are Quaternary. The Brazilian earth near Fortaleza occurs mostly in small lagoons and sand dunes, which may be permanently or intermittently under water.

The source of silica for the great diatomaceous deposits has been considered by numerous geologists. Since diatoms are aquatic plants, the silica to be utilized must be in solution or the organisms must have the capacity to extract silica from suspended silicates, such as clay. Nearly all natural waters contain some dissolved silica and, since it appears that diatoms have limited capacity at least to extract silica from suspended silicates, it is believed that these sources are sufficient to ac-

count for the growth of diatoms as usually found today and possibly also for some of the smaller fossil deposits. It is doubtful, however, whether these sources could be adequate to explain the more extensive deposits, particularly those of the Miocene period. It must be assumed, therefore, that when these great beds were laid down the waters contained relatively high concentrations of dissolved silica.

A relationship between volcanism and diatomaceous sediments was advanced by Whitney,⁷¹ who pointed out that silica in available form could be supplied by volcanic agencies in the form of ashes, pumice, etc. Taliaferro⁶⁹ has elaborated this viewpoint and has associated the Miocene deposits with contemporary submarine volcanism. Bramlette⁶⁴ confirms this opinion.

DISTRIBUTION OF DEPOSITS

Deposits of diatomite of varying degrees of purity and size are found rather widely but not extensively throughout the world. The listing given here is restricted to deposits of current interest. Some important recent references to diatomite localities are given in the bibliography.

United States

California—The world's most important deposit is near Lompoc, northern Santa Barbara County, California. Others are in the Palos Verdes hills, Los Angeles County; near Bradley and Monterey, Monterey County; along the Pit River in Shasta County and various other counties, including Orange, Sonoma, Siskiyou, Plumas and Stanislaus.

Oregon—The deposit near Terrebonne, Deschutes County, Oregon, is the most important in the state. There are numerous other deposits, including those in the John Day Valley, in Otis Basin and in the Klamath Falls district.

Washington—The deposit near Kittitas, Washington, is of most current interest, but there are many others, particularly in Grant County and in the Puget Sound area.

Nevada—There are a large number of deposits throughout the state of Nevada. Properties being operated are near Basalt and Clark. The Carlin, Lovelock and Reno districts have numerous deposits.

Idaho—Numerous undeveloped deposits are in the southwestern counties³³ of Idaho. The largest appears to be 58 miles southwest of Grandview, in Owyhee County.

Maryland and Virginia—Deposits in Maryland and Virginia are mostly along the Patuxent and Rappahanock Rivers.

New Hampshire—Numerous small bog deposits occur northeast and southwest of Lake Winnepesaukee and near Lake Umbagog, New Hampshire.

New York—Adirondack bog deposits in New York occur particularly in Herkimer County.

Massachusetts—In Massachusetts, deposits occur south of Boston on the Neponset River.

Florida—Bog deposits occur in Lake and Polk Counties, Florida, and east of Pensacola.

Other States—There are undeveloped deposits in Utah, Arizona and New Mexico. Small Pliocene and Pleistocene deposits have been reported in the High Plains region of West Texas.²³

Small undeveloped deposits are known in Maine, Vermont, New Jersey, South Carolina, Alabama and Georgia.

Canada

Fossil fresh-water deposits are found along the Fraser and Quesnel Rivers in British Columbia. The principal bog deposits in Canada are in Nova Scotia (New Annam and Digby Neck). Numerous small lake deposits occur in Charlotte County and elsewhere in New Brunswick. Smaller deposits are in Quebec and Ontario, and on Vancouver Island.

Mexico

Fossil fresh-water deposits are in the states of Tlaxcala, Jalisco and Michoacan, Mexico. Marine Miocene localities are on the Revillagigedo and Las Tres Marias Islands and in Lower California.

South America

Brazil—Surveys in Brazil during the past 15 years have shown that many deposits occur in the states of Rio de Janeiro, Maranhão, Pernambuco, Rio Grande do Norte and Ceará.^{17,18}

Chile, Peru and Argentina—Deposits occur in the provinces of Tacna, Valparaiso, and Nuble, Chile; also in the Atacama desert and on Chiloe Island and near Arequipa, Peru. There are some undeveloped deposits in Argentina.

Europe

Denmark—Deposits occur on the islands of Mors and Fur, also at Hollerup and Fredericia, Denmark.

Germany—The Hannover deposits, Germany, on the Lüneburger Heide, are in four districts: (1) near Unterluss, (2) at Munster, (3) along the Luhe River and (4) near Suderburg. Other deposits are in the Vogelsburg, Hesse, in Lausitz, Saxony, and in Klieken, near Coswig in Anhalt.

France—In Department of Cantal, France, near Auxillac, Joursac and Celles, and in the Departments of Puy-de-Dôme, Haute-Loire, Ardèche and Aveyron, there are diatomite deposits.

North Ireland—Along the Bann River, Ireland, in Londonderry and Antrim counties, diatomite occurs.

Spain and Portugal—In Spain, there is diatomite near Elche de la Sierra, in the province of Abacete, and in the provinces of Castille, Seville and Cordoba. Diatomite occurs in the district of Samtarem and elsewhere in Portugal.

Italy and Other Countries—There are deposits of diatomite near Santa Fiora, Bagnolo, Castel del Piano and at Monte Amiata, Tuscany, in Italy. Small deposits, which have been operated or which are of some commercial interest, occur in Sweden, Norway, Finland, Yugoslavia, Rumania, Austria, Czechoslovakia, and Hungary. Small-scale commercial operations have been carried out recently or have been considered at deposits in Sweden, England, and Scotland.

Other Countries

Soviet Union—Diatomite resources appear enormous in various parts of the Soviet Union. Numerous deposits have been reported in the Leningrad area, on the Kola Peninsula, in the central Volga districts, in the Urals, in Transcaucasia and in Georgia. These deposits are of different types, but apparently none are of unusually high quality.

Africa—Large deposits occur in the province of Oran, Algeria, the more important of which are near St. Denis du Sig, Cassaigne, Ouillis and Pont du Chelif. Exploitation of the extensive deposits in Kenya has been attempted.¹⁵ In the Union of South Africa small deposits are found near Krugersdorp, in Zululand and in Cape Province.¹⁶

Japan—A great many localities have been investigated^{26,31} in Japan. These occur as Tertiary marine deposits on the island of Hokkaido. The numerous localities on Karafuto, Honshu, Kyushu and Oki Islands, in Korea and on the Noto peninsula (near Wajima and Wakura) occur mostly as thin, stratified layers in Quaternary sediments.

Australia, Tasmania, and New Zealand—Numerous deposits occur in Queensland, New South Wales, Victoria and Western Australia; also in Tasmania and New Zealand. Many of these occurrences have been known for years, and have been adequately described in various publications.²¹

Java and Other Places—Low-quality diatomite occurs near Cheribon in Java, in Sumatra, in Central Anatolia, Turkey,¹⁹ and in some parts of China.

POLITICAL AND COMMERCIAL CONTROL, PRODUCTION AND CONSUMPTION

Most requirements for diatomite have been supplied by large individual companies or by trade organizations. Thus, in the United States, the Celite Company and the Johns-Manville Corporation pio-

neered the industry and continue to supply the greater tonnage for domestic consumption and also considerable tonnages for export shipments, particularly for filtration and filler uses. The Great Lakes Carbon Co. and the Eagle-Picher Co. operate western deposits. Production in Canada has decreased since 1935.

In Germany the Vereinigte Deutsche Kieselguhrwerke G.m.b.H., Hamburg, has largely controlled the production and marketing of kieselguhr. It represents a trade organization correlating the production of numerous works, principally in the Lüneburger Heide district. In France is La Société de Silices Fossiles de France, at Paris, which controls much of the Algerian diatomite. In Denmark, Moler Products, Ltd. and Mors-Moler largely control the industry. In Soviet Russia production and shipping is controlled by the Government. Private companies operate in North Ireland, Spain, Australia, Italy, Japan, and other countries.

In the United States and Canada many minor companies and organizations have operated different deposits at different times. While most of these have been of temporary existence, with many ownership changes, some of the smaller producers have operated for many years and have been successful in specialties. A feature of the diatomite industry in the United States has been a rather high degree of technical proficiency in product and process improvement, development of new uses and in maintenance of technical service to the consuming industries.

In North America, and to some extent elsewhere, the trade has come to expect distinct uniformity of grade and high-quality standards in diatomaceous products, except where they are used locally or are utilized in the cheaper fields of building materials, ceramic insulations and concrete. The present developed resources in the United States still appear adequate to meet all requirements for many years to come.

The production of diatomite in the United States remained low until about 1915, when operations at the Lompoc deposit began to develop in line with modern industrial requirements. New uses, particularly in filtration, high-temperature insulations and fillers were developed, and standardized products for the various usages were provided. Production since that time has increased steadily except during the depression years of 1930 to 1934, inclusive, when sales for insulation and building materials dropped considerably. During this period, however, the direct-consumption industries continued to require substantial tonnages of filter aids and fillers.

The World War II period saw great advances in the uses of diatomite. Industrial uses for filter powders increased substantially in most of the previously established applications and important new uses became established. Some of these filtration developments were water

for military, municipal and industrial purposes, electroplating solutions, cutting oil emulsions, wort in the brewing of beer, alginates, pectin, various food products and biologicals, particularly penicillin and streptomycin. In filler fields, increased usages of diatomite were in paints (particularly wartime camouflage), paper manufacture, insecticides, treatment of ammonium nitrate for fertilizers, catalyst supports and as a porous litter material for poultry and animals. In building materials increased tonnages were used in the fabrication of sheetings and in fireproof and insulating products of various types.

Published production statistics for diatomite have been incomplete and somewhat confusing. Early records are particularly unsatisfactory. Since the figures that have been compiled may be obtained from government publications and other books readily accessible, they are not duplicated here. Production in the United States since 1921, in three-year periods, is shown in Table 2. World production figures for diatomite are given in Bulletins of the Imperial Institute and were included in former years in *The Mineral Industry*, published by the McGraw-Hill Book Co. Today, the leading producing nations are the United States, Germany, Denmark, Soviet Union, Brazil, Algeria, Japan, Korea, and France. Not unimportant quantities are produced in North Ireland, Spain, Australia, Canada, Italy, and Hungary. Minor producers are Norway, Sweden, Chile, Netherlands Indies, Mexico, and Portugal.

The greatest diatomite resources, undeveloped or in reserve, are in the United States, Denmark, the Soviet Union, Japan, Korea, Algeria, Germany, Kenya, Brazil and, to a lesser extent, Canada. Of all these,

TABLE 2—*Production of Diatomite in the United States*

SHORT TONS

Years	In Three-year Period	Average per Year
1921-1923	162,768	54,256 ^a
1924-1926	219,331	73,110 ^a
1927-1929	286,426	95,475 ^b
1930-1932	248,273	82,758 ^b
1933-1935	244,342	81,447 ^b
1936-1938	279,645	93,215 ^c
1939-1941	360,502	120,167 ^c
1942-1944	524,872	173,957 ^c
1945-1947	675,000	225,000 ^d

^a From *The Mineral Industry of the British Empire and Foreign Countries—Diatomaceous Earth*. Imperial Institute. His Majesty's Printing Office, London, 1928.

^b From *Minerals Yearbook*, 1935. U. S. Bur. Mines. Government Printing Office, Washington, 1935.

^c From *Minerals Yearbook*, 1946. U. S. Bur. Mines. Government Printing Office, Washington, 1948.

^d Unofficial estimate.

the greatest quantity of good quality material is distinctly in the United States. Only unimportant quantities of the best quality of filter and filler material have come from Denmark, Soviet Union, Japan or Algeria. The chief importing nations at present are the United Kingdom (Australia, England, Ireland, India), Canada, France, Norway, Poland, Cuba, Peru, Italy, Yugoslavia, Argentina, and Java. Some important aspects of diatomite production since 1937 are as follows:

1. Leading position maintained by the United States.
2. Germany apparently losing ground in relative world position prior to war, but making some progress in improved processing. Reserves not certain for long-term future.
3. Danish exports of crude earth for manufacture of building materials in England resumed after war.
4. Production increasing greatly in Russia.
5. Brazil using large tonnages for local building materials. May be of future importance as an exporting nation.
6. Japan was able to meet most of its considerable industrial requirements by use of lower grade Japanese and Korean earths.
7. Various small Australian deposits were operated, meeting Commonwealth's requirements for some uses; imports from USA required for filter aids.
8. Kenya diatomite deposits started to produce and may be factor in world trade.
9. Small-scale production in Sweden and Finland, mostly for use in ceramics and building materials.
10. Wide acceptance of diatomaceous filter aids for European sugar manufacture, particularly in Poland, Czechoslovakia, Germany and Russia.

The outlook for the industry is considered favorable. Development of new applications, expansion of established uses and new technologic advances in processing should increase the production and sales of diatomite steadily for many years to come. The trend toward larger tonnages continues as a total of numerous increases in the individual uses, and not to single new uses of large magnitude. Broad expansion of the industry is not expected.

PROSPECTING, EXPLORATION AND MINING

In the dry, compact, stratified deposits, samples may be obtained from the surface outcrops and examined microscopically, physically or chemically. The purer beds are thus determined. Diatomite lends itself to core drilling readily and in some places prospecting is done in this manner. In others, trenches, tunnels, and vertical shafts of narrow cross sections are used to examine the diatomite away from surface con-

ditions of alteration and leaching. These are more satisfactory methods of examination because of the ease with which the diatomite can be excavated. The openings permit a careful examination of the appearance of the material, its stratification, compactness, and inclination of beds. In the wet bog, lake, or swamp deposits, auger drills are often used, so that one foot of material can be brought up at a time. For underwater sampling, a casing is driven into the mud and boring is done inside the pipe. Tonnages are based on the amount of dry material in a cubic foot of the earth.

The usual practice in the United States is to quarry the compact beds of diatomite with power shovels. Underground methods are also employed, using shrinkage or room-and-pillar mining. In the western United States little timbering is required providing adequate pillars of diatomite are left to support the roof. At Lompoc, California,²⁹ diesel and electric shovels load diatomite in the quarries into huge dump trucks, which haul to vertical storage shafts. Underground, 14,000 ft of tunnels is electrified for hauling to the milling plants.

In eastern Canada and northeastern United States, the diatomite is recovered from bogs, lakes and swamps. It is mined by dredging or by preliminary draining. After the water has been drained off, recovery is by hand shoveling into dump cars, by bucket dredges, or by suction dredges. The wet diatomite is piled up to drain off free water, then spread out to air-dry before treatment.

PREPARATION FOR MARKET, TESTS AND SPECIFICATIONS

The method of preparation for market depends on the mode of occurrence, composition, and uses intended. In Denmark the impure, clayey material is simply milled and used for fabrication of ceramic articles (industrial and building). When it occurs in recent deposits, as in peat bogs or ponds, the material is dredged, classified, dried and calcined (as in New York state and Florida). When it comes from pits, as in the Lüneberger Heide, the material is dug, mostly by hand, calcined in lump form (or in special furnaces), elutriated, classified, and otherwise treated.

In the western United States deposits, the crude earth from open quarries or cuts is field-dried to some extent and then transported for milling. Producers of large quantities have equipment and processes for drying or for drying and milling simultaneously. Diatomite products may be classified broadly as brick or block, crushed aggregates and pulverulent powders. Diatomite brick, with clay or other binders and with or without organic filler to be burned out, are fabricated with conventional equipment—blending bins, puggers, presses, driers, kilns, sizing equipment, and so forth. The principal manufacture of brick and pressed block is in the United States, England, Germany, Brazil

and Austria. Aggregates are prepared by crushing, screening, and grading.

In the preparation of diatomaceous powders, the crude (field-dried or wet) is conveyed to storage system or directly to trommel screens or grizzlies, then to primary crushers, mechanical traps for removal of rock, trash, flint or coarse impurities of any kind, thence to driers or to the secondary mills in combination with driers, thence to air classifiers for removal of finer grit and foreign matter and sometimes for classification according to particle size. Many types of primary crushers may be employed. For secondary milling, mills on the swing-hammer principle or centrifugal fans are preferred. Some products are calcined and treated chemically; the dried powders go to rotary or stationary kilns or to treatment tanks. Following either heat or chemical treatment, final dispersion of the powders is generally necessary, and this is accomplished by special mills or blowers. In some instances, further purification and classification is effected pneumatically, subsequent to calcination. Water classification is carried out to some extent in Germany.

An idealized and simplified flowsheet is shown in Fig 5 for "dry" deposits in western United States. A pictorial flowsheet for Lompoc operations⁶² gives some further detail. Bureau of Mines investigations⁶¹ on the beneficiation of low-grade diatomites by froth flotation have shown promise, but costs appear high for most commercial operations. Vogeler⁶³ and Cummins²² reviewed methods of mining and processing in Germany.

Tests and Specifications

Crude diatomite is evaluated on the following properties: freedom from impurities (sand, volcanic ash, crystalline silica, organic matter, clay, lime, soluble salts, etc.); microscopic structure (types of diatom forms and their condition, whole or broken, and relative proportions of different diatom forms); presence or absence of exceedingly fine particles; apparent or bulk density; friability (behavior on milling); color; opaline silica content.

The value of diatomaceous products is determined by: microscopic structure, bulk density (loose, tamped or on vibration); absorptive capacity (water, oil or other liquids); chemical composition (iron, alumina, manganese, rare metals, alkalies, organic matter, etc.); specific gravity; sieve analysis; particle size; color; thermal conductivity; moisture (free); combined water and special tests such as filtering efficiency and workability as admixture. Testing techniques for filter aids have been described by Cummins and Weymouth.³⁸ Testing procedures have also been given in a publication by Skinner et al.³⁴

Specifications for diatomaceous products vary greatly because of the wide diversity of uses and requirements. For low-priced crude near

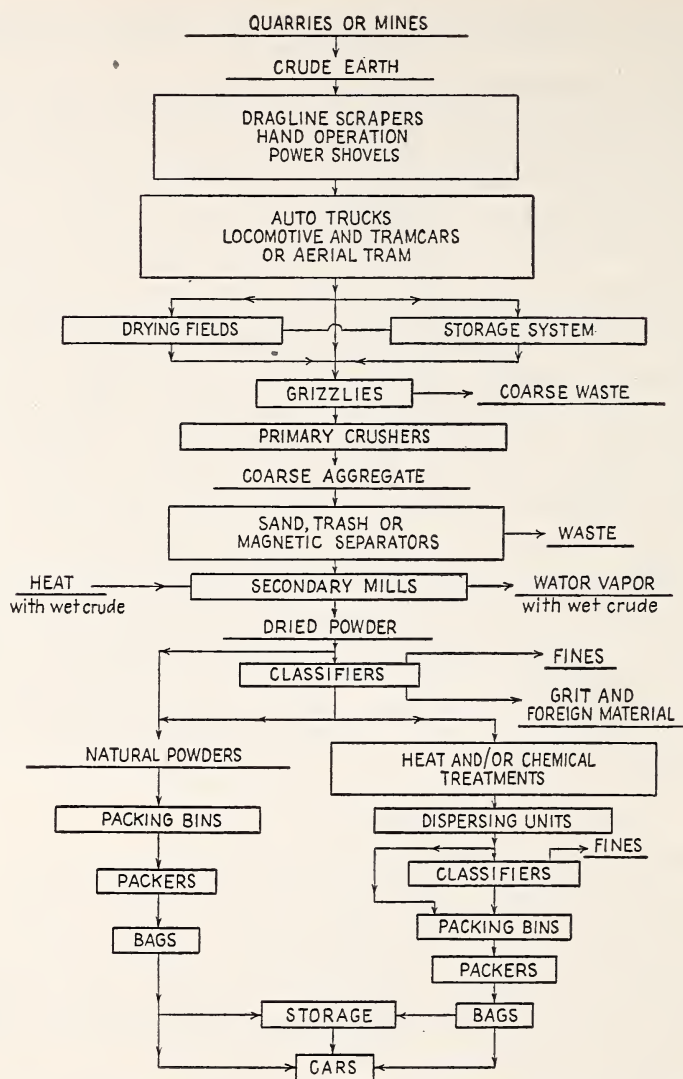


FIG 5—FLOWSHEET OF DIATOMITE PLANT IN WESTERN UNITED STATES.

sources of supply, the only requirements are bulk density and moisture content. For some specialized filtration and filler uses, definite chemical and particle-size specifications are required. For some polish and abrasive uses there are exacting requirements for mesh size and freedom from grit. For some filler uses, there are equally stringent requirements for color and particle size. Many customers have set up special requirements that are not publicized. There are several government specifications, particularly for insulating materials, admixtures and fillers. The principal producers also have supplied specifications for many of their

products. It is frequent practice to substitute standard samples in lieu of written specifications, and for many diatomaceous products this is recognized as good practice.

Detailed specifications for diatomaceous products cannot be given here, but the following may serve as guides in indicating the properties considered most important for different general uses: **INSULATING COMPOSITIONS**—Apparent density (brick, block, etc.); bulk density (aggregates and powder); microscopic structure; mesh or sieve analysis (aggregates, granules and powders); thermal conductivity; moisture. **FILTER POWDERS**—Microscopic structure and particle size; chemical purity and inertness; low density; filter performance. **FILLERS**—Chemical purity and inertness; particle size and microscopic structure; fineness and freedom from grit; color; absorptive capacity. **ADMIXTURES**—Reactive silica; chemical composition; fineness; workability.

MARKETING

The important sources of diatomite are generally distant from the principal markets, and since the material is bulky, freight charges are high. Packaging costs also are high, since care is required in packing and shipping because of the fragile nature of brick and possible injury to the structure of powders. Diatomite materials are seldom shipped in bulk, although crude may be so handled. The greater tonnage of diatomaceous products is purchased in carload quantities.

USES

The uses of diatomaceous silica in order of importance have been estimated as follows: filtration 50 pct, insulation 25 pct, fillers admixtures and miscellaneous 25 pct. The more important uses are:

Filtration—Diatomite is used in filtering raw cane sugar and in refining; in beet-sugar manufacture, and with molasses, corn sugar and glucose, maple sirup, beer and wort, wines, distilled spirits and liquors, fruit juices and beverages (grape, prune, cider, citrus), fruit pulps, pectin, malt products and extracts, water (military, municipal, boiler-feed and other industrial waters, swimming pools, etc.), dry cleaning, mineral oils and petroleum products, vegetable oils, animal oils and fats, liquid soaps, gelatin, glue and adhesives, chemical solutions, electroplating solutions, salts and salines, titanium pigments, metallurgical slimes and solutions, cutting oil emulsions, sewage, gas purification, pyroxylin and cellulose acetate, varnishes and lacquers, trade wastes and effluents, rigid filters (bacterial, etc.), porous diaphragms, separators, etc., flavoring extracts, vinegar, hydrogenated oils, alginates, starch pastes, sizing, etc., dyestuffs, used crankcase oils, analytical and laboratory uses, serums and antitoxins, perfumes, extracts, pharmaceuticals and cosmetics, penicillin, streptomycin, vitamin extracts, et cetera.

Insulation—Diatomite in its various forms is widely used for industrial heat and cold insulations: power-plant equipment, in steel and nonferrous metallurgy and heat-treating, petroleum refineries, glass manufacture, ceramic kilns and equipment, gas-generating equipment, ovens, furnaces, kilns, pipe covering, refrigerators, cold-storage buildings, metal annealing, etc. The common types of products used are block, brick and slabs, aggregates, powders and cements. Brick may be "natural" as cut from the deposit or fabricated, with or without inorganic binders and with or without additional porosity, as by burning or melting out organic matter. Block and pipe covering are molded with bonding agents, fiber, magnesia, and other substances. Cast compositions are made with aggregate or powder and a hydraulic bonding agent such as cement, gypsum, or magnesia. Mortars, cements, and so forth are made up with bonding agents, fiber, etc., and usually mixed with water and applied on the job. For metal annealing, powder is generally employed. For cold-storage warehouses and low-temperature insulations, block, aggregate or powder is commonly used. In building and home insulation for both heat and sound, powder, granules, blocks, sheets, are standard forms.

Fillers—Diatomite is used as absorbent for acetylene, in battery-box compositions, molded asphaltic compositions, roofing, flooring, waxes, paints (camouflage, flat paints, oleo-resinous paints, etc.), varnishes, lacquers, pigments, catalyst supports (hydrogenation, oxidation, Fischer-Tropsch), fuses and explosive caps, rubber, match-head compositions, natural and synthetic plastics, sulphur, dynamite and other explosives (for instance, liquid oxygen), polishes (silver, metal, automobile, cake, liquid, paste), carrier for chemical reactions, fire-resistant compositions, absorbents, insecticide diluents and grinding DDT, paper (wall-paper, blotting, filter, glassine, printing, pitch control), abrasives (glass, cleansing compositions), absorbent for radioactive emanations, safe filler, linoleum, artificial leather, sealing wax, glue, artificial stones, pharmaceuticals and cosmetics, putties, packings, to prevent caking and hardening (particularly ammonium nitrate for use as fertilizer), mold wash, soaps, phonograph records, printing inks, absorbents for disinfectants, drying agent, fertilizers, dental investitures, and many others.

Miscellaneous—Diatomite is used in manufacture of soluble silicates, ultramarine, glazes, enamels, as fine reactive silica for chemical processes, manufacture of oil-decolorizing products and synthetic silicates, poultry litter, floor-sweep granules.

Building Industry—In the building industry, diatomite is used as admixture for concrete, mortars, cements and plasters; as a constituent of high-silica and puzzolan cements and as a replacement for portland cement in certain concretes; in flooring, pavements, roads, roofing, light-

weight building brick, blocks, slabs, wallboard, panels. Diatomite is a preferred source of silica in the manufacture of lime-silica insulating and building materials.

PRICES

Prices for diatomaceous products remained relatively constant from 1918 until the late 1930s. The increased costs of fuel, labor, and equipment from 1920 to 1930 were offset to some extent by improvements in processes and greater production. Cost trends were slightly lower in the depression years 1930 to 1935. Since 1935, operating costs have increased materially because of high costs of labor, fuel, equipment, and containers for the finished products. Prices, however, continued comparatively stable until 1945 and 1946 but since that time increases in general have been 20 to 40 pct above prewar levels. Detailed sales prices are difficult to give, since the price range is broad, depending upon the source of the diatomite and the degree of processing necessary to prepare it for the market. Crude diatomite at the deposits is cheap, \$5 per ton upward. The average for the years 1942 to 1944 was given in the Minerals Yearbook as \$18.85 per ton. Milled or processed powders range in price from \$15 to \$60 per ton at the milling plant. The "average" quotation for domestic, purified diatomite, c.l., Atlantic seaboard, was given for May 1948 by *Chemical and Engineering News* as \$62 per ton. Highly purified or specialty grades sell for \$100 or more per ton at the production point. Insulating brick produced in the United States range in price from \$60 to \$120 per thousand at the shipping point.

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CHAPTER 14

DIMENSION STONE

BY OLIVER BOWLES*

DIMENSION stone is a convenient term applied to stone sold in blocks or slabs of specified shapes and usually of specified sizes, as contrasted with crushed, broken and pulverized stone, discussed in another chapter. Dimension stone includes cut stone, rough building stone, ashlar, rubble, paving blocks, curbing and flagging. Riprap—large, irregular blocks used for shore protection—is classed more properly with crushed and broken stone.

COMPOSITION, VARIETIES AND PROPERTIES

Stones used as blocks or slabs are of many kinds. The principal varieties are granite, sandstone, limestone and marble. Slate is covered in another chapter. Granite is a visibly granular crystalline rock consisting essentially of feldspar, quartz, and mica or hornblende. Limestone consists essentially of calcium carbonate, with which may be associated certain impurities such as clay, sand, or iron oxide. Dolomites and magnesium limestones used as dimension stone are classed with the high-calcium limestones, as they are used in the same way. Marble is a crystalline form of limestone. Sandstone consists essentially of silica in the form of sand grains cemented together into a coherent mass.

Although rock occurrences are numerous and widespread, the exacting requirements of use condemn all but a small fraction of them for commercial use as dimension stone. No deposit that has closely spaced cracks, lines of weakness, or joints can be so used because sound blocks of moderate to large size are demanded. Uniform texture and grain size, constant and attractive color, and freedom from impurities that may cause stains or deterioration usually are required also.

Hardness is a variable property. Granites are as hard as or harder than steel while limestones and marbles may be scratched easily with a knife. The hardness of a sandstone depends upon the degree of cementation of the grains. Workability depends to a considerable extent on hardness, but the degree of hardness has little influence on use except when stones are subjected to severe abrasion, as on steps or floors.

“Texture” as applied to stone relates to the arrangement, uniformity, and size of the constituent grains.

* Consultant in Nonmetallic Minerals, Washington, D. C.

Stones are of many colors and thus can satisfy a variety of tastes. For monumental stone, a marked contrast between polished and tooled surfaces is preferred in order that inscriptions may be read easily.

Strength requirements usually may be disregarded because any sound structural stone suitable in other respects is almost invariably many times as strong as would be required for any ordinary use. The pressure on the base course of the Washington Monument, Washington, D. C., which is 555 ft high, is less than 700 psi, and high-grade granites, limestones, sandstones and marbles will sustain a crushing load of 10,000 to 25,000 psi. A structure made of stone with a crushing strength of 15,000 psi would have to be nearly $2\frac{1}{2}$ miles high before crushing of the lower courses would occur. However, stone disintegrates more readily under severe stress, therefore a safety factor of 20 is demanded usually. A crushing strength of 5000 psi is considered satisfactory for all ordinary uses.

Porosity, expressed as the percentage of pore space to total rock volume, ranges from 1 to 10 pct for commercial sandstones and from 0.5 to 5 pct for limestones, while marbles, granites and slates may run lower than 0.1 pct. The specific gravity of common rocks ranges from 2.2 to 2.8 and the weight per cubic foot from 140 to 180 lb. Details of the physical and chemical properties of stones from many localities are given by Parks,³³ Merrill,^{28,29} and Kessler.^{21,23,24}

ORIGIN, OCCURRENCE AND DISTRIBUTION OF DEPOSITS

Igneous rocks have been generally regarded as originating from molten masses or magmas but recently it has been claimed that some of the so-called igneous rocks have resulted from the action of hydrothermal waters of magmatic origin. Slow cooling of magmas or other reactions deep within the earth resulted in coarse crystallization of the constituent minerals. The principal rock type of this class is granite. Magmas that cool more rapidly form finer-grained rocks, such as basalts and aplites.

Sedimentary or stratified rocks are those laid down in strata or layers. The materials forming them are derived from the disintegration of pre-existing rocks. Vast quantities of the products of rock decay are carried by water and ice and deposited as sediments in oceans, lakes and river beds. In addition to this detrital material, millions of organisms that inhabit oceans or lakes secrete calcium carbonate or silica from the water to form their shells and their skeletal remains add to the accumulation. The principal rocks thus formed are sandstone, limestone, and shale, but the latter, because of its easy disintegration, is not used as dimension stone.

Most sedimentary rocks used commercially as building stone have suffered little deformation and therefore occur as horizontal or nearly horizontal beds. In many places, however, the great mountain-building

forces ever at work within the earth have squeezed, crumpled, and folded the sediments. Heat and pressure may bring about a rearrangement and crystallization of the constituent minerals, forming new types known as metamorphic rocks. Thus, limestones are converted into marbles and sandstones into quartzites. Marbles are used widely for structural and ornamental purposes but quartzites, because of their excessive hardness, are used sparingly. Slates, covered in another chapter, are formed by intensive metamorphism of shales.

The Appalachian district of eastern United States, extending from Maine and Vermont to Georgia, is a rugged, mountainous region in which igneous and metamorphic rocks abound. There are important deposits of granite, marble and slate in this territory. The great area lying between the Appalachian belt and the Rocky Mountains is characterized chiefly by nearly horizontal sediments that are well represented by the famous limestone deposits of Indiana and the well-known sandstones of Ohio. Important granite outcrops also occur in this area, notably in Minnesota, Wisconsin, Missouri, and Texas.

In the Rocky Mountain belt, numerous igneous and metamorphic rocks occur and from this belt to the Pacific Coast igneous rocks prevail. Limestones also occur and have been metamorphosed into marbles in places. Vulcanism of comparatively recent geologic age has produced lavas, rhyolites, and volcanic tuffs that rarely occur in the eastern or central states.

Building and ornamental stones abound in many foreign countries. Notable examples are the marbles of Africa, Italy, France, Belgium, and England; the granites of Scotland, Finland, Norway, and Sweden; the granites and marbles of Canada; the travertine of Italy; the onyx marble of Mexico. Many of those occurring in the Old World were used in ancient times for building pyramids, obelisks, temples, and other classic masterpieces of Greek, Roman, and Egyptian art and architecture. Although many are now in ruins, they furnish valuable data on the culture and mode of life of ancient peoples.

POLITICAL AND COMMERCIAL CONTROL

Stone deposits for the most part are owned and operated by the nationals of the respective countries in which deposits occur. Most countries in an emergency would be self-sufficient, although under normal conditions of trade a good deal of stone crosses international boundaries. Many varieties have no counterparts outside their own restricted areas, and on this account they are conveyed long distances to satisfy the demands of architects, builders, and manufacturers of memorials.

PRODUCTION AND CONSUMPTION

Statistics of the stone industries of the United States are based on sales. Stocks of finished products on hand are an unimportant factor;

therefore production and consumption may be regarded as virtually equal. Table 1 shows sales of dimension stone during certain representative years. The striking decline since 1926 indicates the inimical effects of depressions and wars on the dimension-stone industries.

TABLE 1—*Sales of Principal Varieties of Dimension Stone in United States during Certain Representative Years^a*

Stone	1926		1936		1946	
	Short Tons	Value	Short Tons	Value	Short Tons	Value
Granite . . .	1,588,970	\$23,224,502	666,850	\$11,096,744	535,230	\$16,712,268
Marble . . .	335,950	13,467,796	97,800	5,532,821	77,010	7,081,015
Limestone .	1,661,260	21,004,024	804,710	4,918,184	504,070	5,878,904
Sandstone .	544,380	5,839,709	162,450	1,655,671	160,900	2,327,078
Total . . .	4,130,560	\$63,536,031	1,731,810	\$23,203,420	1,277,210	\$31,999,265

^a Minerals Yearbook, U. S. Bureau of Mines.

Fig. 1, based on statistics of the United States Bureau of Mines, shows trends in sales of building and monumental stone during recent years. Fig. 2 shows trends in sales of building stone, by kinds, for a series of years. The low level of sales since 1930 reflects the unprecedented stagnation during the industrial depression and the war in construction of type of structures in which stone is used as a major building material. Detailed statistics of the dimension-stone industries are published each year by the United States Bureau of Mines in the Minerals Yearbook.

PROSPECTING, EXPLORATION AND MINING

A small fraction only of the innumerable rock deposits scattered in every part of the country yields suitable dimension stone; therefore very careful exploratory work should be done to assure a sufficient supply of satisfactory material before money is spent by a prospective operator for development. If the rock appears in bare outcrop, the exposed surface should be examined carefully, and enough rock should be removed to permit examination of a fresh surface below the zone of weathering. The features to which most attention are given are freedom from cracks or closely spaced joints, uniformity of texture, attractiveness of color, and for some uses, capability of taking a polish.

Surface exploration should in most instances be supplemented by core drilling. The drill cores usually are 3 in. or smaller in diameter. In flat-lying beds prospect drilling is simple and the holes may be widely spaced, that is, 100, 500 or even 1000 ft apart. Where beds are

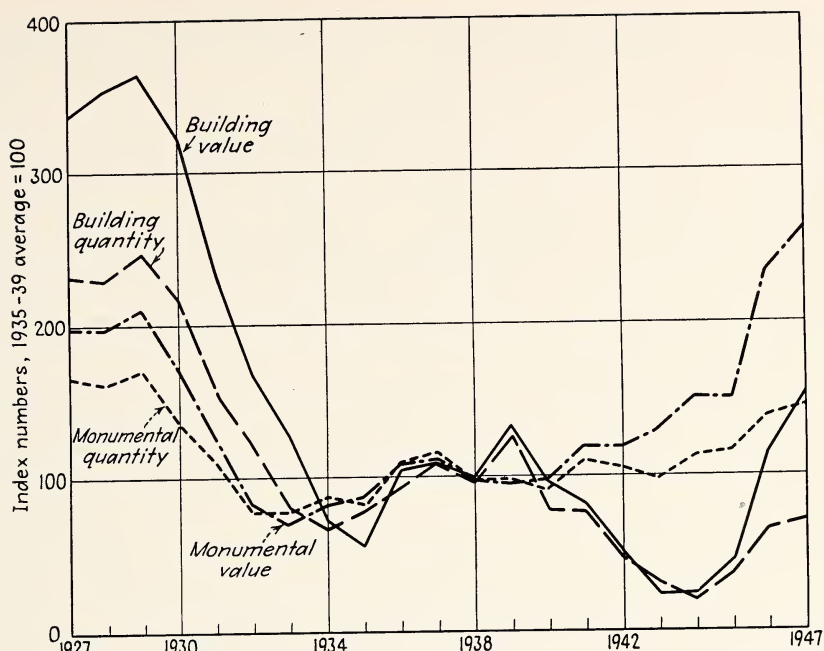


FIG 1—QUANTITY AND VALUE OF BUILDING AND MONUMENTAL STONE SOLD IN THE UNITED STATES, 1927-1947.

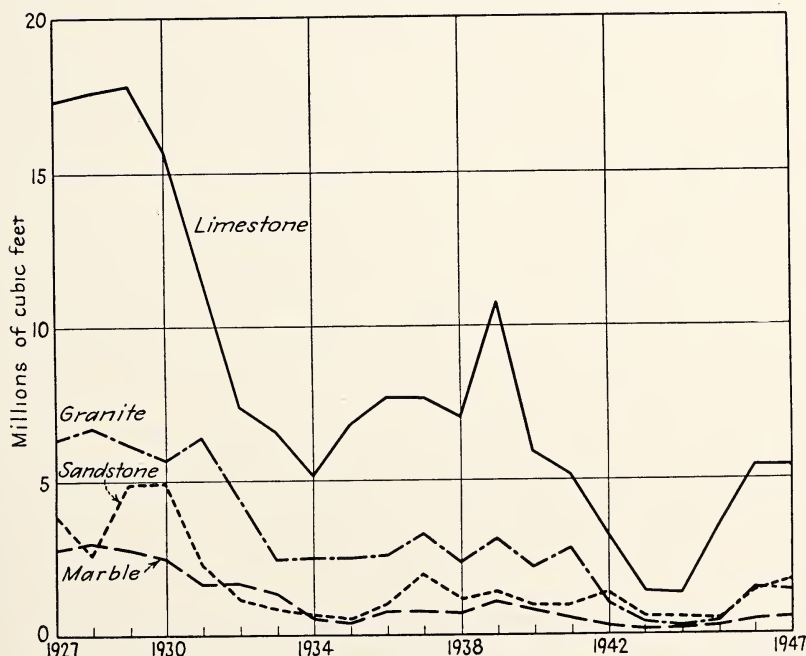


FIG 2—QUANTITY OF BUILDING STONE SOLD IN THE UNITED STATES, 1927-1947, BY KINDS (RUBBLE NOT INCLUDED).

folded or faulted, a thorough study of the structure should be made with the aid of geologic maps. The position, thickness, and slope of the beds is first determined and the drill holes usually are sunk at right angles to the beds. Accurate records are made of each hole and as the core sections are removed they are marked, recorded, and stored for future study.

Granite deposits usually are fairly uniform over considerable areas and their depth, with few exceptions, is very great. Generally, therefore, prospect holes may be widely spaced. Core drilling with shot or diamond drills costs \$3 to \$5 a foot, depending on the nature of the rock and drilling conditions.

Stripping—Stripping is the process of removing the overburden of clay, gravel or sand from the rock surface. If a considerable volume of material is to be moved, mechanical methods usually are employed. The hydraulic method is the most economical but it can be used only where an ample supply of water is available, where a waste-disposal area is situated favorably, and where the overburden is friable enough to be washed down and carried away with a stream of water. Dragline scrapers or excavators, power shovels, clamshell buckets operated from derrick arms, tractor excavators and scrapers are other types of mechanical equipment used. For removal of thin overburden, particularly on rugged rock surfaces, hand methods must be used. The cost of power-shovel stripping ranges from 15¢ to 50¢ a cubic yard, depending upon working conditions and nearness of disposal area.

General Methods of Operation—Two general methods of operation are followed in securing dimension stone—open-pit quarrying and underground mining. Open pits are of two types, the “shelf” quarry and the “pit” quarry. Where the ledge of stone forms a hill, the floor of a quarry worked in the hillside may be little if any lower than the surrounding country. Such an opening is known as a shelf quarry. Both transportation and drainage are favorable in such quarries. Pit quarries are more common. They are sunk below ground level, access is gained by stairs, ladders or mechanical hoists, and material is conveyed from the quarry by inclined tracks, derricks, or cableway hoists. Pits may reach depths of several hundred feet.

If the beds of serviceable stone dip beneath waste rock, or if for any other reason open-pit work is not feasible, underground methods may be pursued. Selective mining can be accomplished best by the underground method; no stripping is required and workers are not exposed to the weather. On the other hand, the cost of making primary openings is high and much material must be left for roof support. A method of quarrying known as “undercutting,” intermediate between the open pit and the tunnel, is sometimes pursued. Channel cuts along the walls have an outward slant, thus the floor space is en-

larged gradually. Wings or buttresses of stone may be left at intervals for wall support.

GRANITE

Granite in the form of dimension stone is produced chiefly in the Appalachian district of eastern United States from Maine to Georgia, and in the middle western states, particularly in Minnesota, South Dakota and Wisconsin. Relatively small quantities are produced in the Rocky Mountain and Pacific Coast states.

The five leading states in order of value of production of building granite in 1946 were Minnesota, Massachusetts, Maine, North Carolina, and South Dakota, and of monumental granite, Vermont, Georgia, South Dakota, Minnesota, and Wisconsin. The six leading states in total value of production of granite in the form of dimension stone were Vermont, Georgia, Minnesota, South Dakota, Wisconsin, and Massachusetts.

Vermont—Granite is produced in Vermont chiefly in the district surrounding Barre and Graniteville, Washington County, and Williamstown, Orange County. The typical "Barre" granite, which is widely used for monuments, is a fine to medium-grained gray to white biotite granite. The darker varieties are most in favor for monument dies and the lighter for buildings, mausoleums and monument bases. In past years, granite was produced fairly extensively at Newark, Hardwick, and Groton, Caledonia County; Derby, Orleans County; Dummerston, Windham County; and Bethel, Windsor County.

Georgia—Building granite, paving blocks and curbing are produced at Stone Mountain and Lithonia, DeKalb County, and memorial granite near Elberton, Elbert County.

Minnesota—"St. Cloud red" and "St. Cloud gray" are well-known memorial granites quarried near St. Cloud, Stearns County. Building granite is also produced in this area. Other producing areas are in near-by Wright and Benton Counties and in several counties in the Minnesota River valley westward to the South Dakota boundary.

South Dakota—The Milbank area, Grant County, has become an important center of monumental and to a lesser extent architectural granite.

Wisconsin—Granites of a variety of colors ranging from black, gray, and pink to brilliant red are quarried in Wisconsin. The chief centers are Mellen, Ashland County; Wausau, Marathon County; Amberg, Marinette County; Montello, Marquette County; and Lohrville, Wausara County.

Massachusetts—The most important producing area in Massachusetts is near West Chelmsford, Middlesex County, where building and monumental stone and curbing are manufactured. Quincy, Norfolk

County, once an important center of memorial stone production, has become of lesser importance. Monumental stone is produced also at Chester, Berkshire County.

Maine—The chief centers of granite production in Maine are Stonington, Hancock County; Clark Island, Knox County; North Jay, Franklin County; Frankfort, Waldo County; and High Pine, York County. Some years ago, Maine was an important source of granite paving blocks but that industry has declined greatly. Building and monumental stone are now the principal products.

North Carolina—Important granite-producing areas are Mount Airy, Surry County, and Salisbury, Rowan County. The principal product is building stone.

Other States—Other active granite centers are Academy, Pomona, and Alhambra, California; Milford and Millstone, Connecticut; Milford and Concord, New Hampshire; Snyder, Oklahoma; Coopersburg and St. Peters, Pennsylvania, where "black granite" (diabase and gabbro) is produced; Westerly, Rhode Island; Rion, South Carolina; and Fredericksburg and Llano, Texas.

Structural Features of Granite

Although innumerable granite deposits occur throughout the country, only a relatively small number of them are of suitable color or texture or are available in sound blocks large enough for use as dimension stone. Most granite deposits are characterized by joints or seams—natural fractures that cut the rock mass usually in a nearly vertical direction. They tend to occur in more or less parallel arrangement, frequently in two major systems intersecting approximately at right angles. If they are spaced closely, the rock is useless for dimension stone, but if regularly spaced 10 to 30 ft apart they are of great advantage in quarrying. Horizontal partings that separate the granite into sheets or layers are known as sheeting planes.

Most granites split in some directions with greater ease than in others. The direction of easiest splitting is known as the "rift." A second less strongly marked tendency to split, usually at right angles to the rift, is known as the "grain" or the "run." The direction at right angles to both rift and grain is called the "hard way" or "head grain." These splitting directions are obscure and can be recognized only by skilled stonecutters, but they are of the utmost importance in processes of quarrying and shaping blocks of granite.

At some period in its history, the granite mass may have been intruded by a rock magma injected into joints or fissures. Such "dikes" are of two kinds—light colored, known as "aplite," and dark colored, consisting of basalt or diabase. Dikes are to be avoided in quarrying and if they are numerous the deposit may be worthless. "Knots," con-

sisting of dark spots, lenses or patches, and "hair lines," fine lines of discoloration that may be either veins or dikes, are also objectionable, particularly on granite to be polished.

Quarry Methods for Granite

The position and direction of quarry walls in granite generally are governed by the joint systems, because an open joint usually forms a "heading" or quarry wall. Fortunately, the rift usually parallels a major joint system.

Drilling is the most important quarry process. Tripod piston drills, widely used in early years, have been displaced generally by hammer drills, which can be moved more quickly and handled more easily. For making rows of closely spaced holes, the bar drill is used. This consists of a horizontal bar 12 to 14 ft long supported by a pair of steel legs at each end. A heavy hammer drill is mounted on the bar and may be moved quickly to any desired position by means of a pinion working in a rack of cogs. At Barre, Vermont, each bar-drill machine averages 100 to 120 lin ft per day for moderately deep drilling, using a $2\frac{3}{4}$ -in. bit as a starter. For shallow holes, hammer drills held in the hands usually are employed.

In opening a new bench on a quarry floor, the most difficult step is to obtain a free face from which to work. A mass of rock 3 to 5 ft wide and the depth of the bench must be removed to give the necessary working space. Different methods are employed to make such a trench. If the mass is flanked on either side by an open seam, it may be removed by drilling and blasting. If open seams cannot be utilized thus, holes may be drilled in two parallel rows 3 to 5 ft apart and the intervening rock shattered with dynamite and removed as waste. Another method is to drill the holes close together and remove the thin walls or webs between them with a flat broaching tool, thus forming a narrow channel. Two such channels may be made parallel with each other and any desired distance apart. When the rock between them is removed, a trench is provided. This method is less wasteful than blasting, for the mass of rock between the channel cuts can be removed in block form and utilized. In some quarries, it is advantageous to use the channeling method for many subsequent cuts. Although this method is more costly than blasting, the waste reduction is more than sufficient to compensate for the additional cost.

The larger masses may be separated from the solid ledge by blasting with light charges of black blasting powder. To facilitate splitting, fractures are made in the directions of rift and grain as far as possible. Subdivision of the large blocks is accomplished by "plug-and-feather" wedging. Holes $\frac{3}{4}$ in. in diameter and 4 or 5 in. deep are drilled in line 6 to 18 in. apart. Pairs of soft-iron plates with steel wedges between

them are placed in the holes and sledged lightly back and forth until a fracture is made. If a break is to parallel the hard way, foot holes 1 to $1\frac{1}{2}$ ft deep are drilled $1\frac{1}{2}$ to 4 ft apart, with shallow plug holes between them. To obtain large, thin blocks suitable for platforms or mausoleum covers, holes are drilled in line about 6 in. apart to almost the full depth of the block and a fracture is made by driving wedges into them.

During 1946 and 1947, experiments were conducted at Barre, Vermont, on the use of the wire saw in cutting granite. This equipment has proved highly advantageous in the slate district of Pennsylvania but the extreme hardness of the rock has discouraged its use in granite. Fair success has been attained in Vermont in subdividing individual blocks and the application of the method to making primary quarry cuts is contemplated. The attainment of a fair rate of cutting without unreasonable wear of the wire used as a cutting tool would mark a new era in quarrying granite.

Blocks may be removed from wide, shallow quarries with tractors, autotrucks, or two-wheeled mule carts. Derricks usually are employed for the deeper, narrower quarries.

Preparation of Granite for Market

The principal granite products are monumental stone, building stone, paving blocks, curbing, and rubble. The term "rubble" is applied generally to rough, irregular building stones having one good face.

Curbing and paving stones usually are shaped on the quarry floor or in an adjacent yard. Curbstones are of two kinds, straight and corner (curved). The latter are the more difficult to make and require more stone and more time and labor. After curbstones are split to approximate size and shape, they are smoothed to some extent with hand tools and finished with pneumatic tools. The part that appears above the pavement when the curb is placed is dressed to a smooth surface but the part remaining underground may be much rougher. Specifications for size and surfacing differ, depending upon city requirements.

In paving-block manufacture, the larger blocks are subdivided by driving plug-and-feather wedges into shallow drill holes and the directions of rift and grain are followed carefully. Final subdivision often is made with a "bull wedge," a blunt steel plug placed between two iron feathers in a shallow notch cut with a pneumatic tool. One blow with a sledge will make the break. Paving stones are made in various sizes. The smaller ones are known as Belgian blocks. Market quotations in New York usually specify 30 blocks to a square yard.

In early years, quarry blocks were dressed entirely with hand tools. These are used still for certain operations but most of the work is done with mechanical tools. The pneumatic tool, with which much smoothing and carving is now done, is guided by hand but the impact is supplied by compressed air.

The "roughing down" of surfaces to a comparatively uniform smoothness is accomplished chiefly with a surfacing machine that consists of a cutting head mounted on a horizontal swinging arm. Cutting tools fitted into the nose of the cutting head are driven against the stone by rapid blows of an air-driven piston hammer. As the cutter is guided over the surface, it chips off fragments and gradually works the stone to a smooth and even surface. By using different kinds of tools, different kinds of surface can be obtained. A four-point tool with a square face on which are four blunt projections gives a rather rough surface. A bush-hammered surface is obtained with a tool consisting of a series of parallel steel plates.

Carving requires much skill and experience. Air-driven tools in great variety are used. A large part of the carving formerly done with hand tools is accomplished now by sandblasting. The rock surface is first coated with a molten rubberlike compound known as "dope," which hardens quickly. Letters or other designs are imprinted on the surface, and with a small sharp tool the dope is removed from all parts that are to be cut below the surface. Powdered carborundum, steel shot, or sand is driven against the surface from a nozzle carrying air pressure of 80 to 100 psi. The sandblast cuts away the stone from all unprotected surfaces. Intricate designs may be fashioned in great detail in a mere fraction of the time required for hand carving.

During recent years, sawing has become an established process in granite mills. The gang saw consists of a series of steel blades set in parallel position in a frame that has a forward and backward motion. Spacing of the blades determines the thickness of the slab or block. Blades that are about $\frac{1}{2}$ in. thick and have notches about one foot apart on the lower edge are fed with steel-shot abrasive. The cutting rate ranges from 4 to 9 in. per hour.

Circular saws 5 to 12 ft in diameter, provided with detachable notched steel teeth, also have been designed for cutting granite. The granite blocks are mounted end to end on cars and the spaces between are filled with plaster of paris, to keep the shot in the cut as the saw passes from one block to another. The rate of travel ranges from $1\frac{1}{4}$ to 5 in. a minute and the saws cut from 25 to 100 sq ft per hour. Sawing is costly but it conserves stone and, as cuts can be made in any direction irrespective of rift or grain, the most attractive colors and patterns attainable may be secured. Also, the surfaces are so smooth that rubbing and polishing are facilitated greatly.

Much memorial and ornamental building granite is polished. Blocks pass through several successive stages of manufacture before a polished surface is obtained. Sawed blocks, or those smoothed with surfacing machines, are set in groups with their upper surfaces on an even plane. They are boxed in and all cracks are filled with plaster of paris. A power-driven rotary head known as a "scroll," consisting of

iron rings or segments, is supplied with steel shot and when guided over the surface wears it smooth. This process is known as "ironing." The next step is to use a lighter scroll with carborundum powder as abrasive. Finer and finer grades are used in succession. This process is known as "emerying." The final stage, known as "buffing," consists in polishing the surface with revolving pads of paper-mill felt supplied with "putty powder"—fine-grained tin oxide. Single blocks are now polished in some mills without setting in plaster of paris. The abrasive is collected in a trough for re-use. Small air-driven portable polishers are used for narrow edges, and curved or irregular surfaces are polished by hand.

The principal surface finishes are rock-faced, hammered, steeled (obtained by ironing with steel shot), and polished.

Silicon carbide wheels are now used generally in granite-cutting establishments to cut moldings, to shape fluted columns, and for similar processes. For making columns, the granite block is first dressed to cylindrical shape and then placed in a lathe. Steel disks chip off projections and gradually work the stone down to a smooth surface. It is then ground with steel shot and carborundum powder and polished in the usual way.

LIMESTONE

Limestones are of many kinds. Some are named after their principal impurities, for instance, siliceous, ferruginous, and carbonaceous.

Oölitic is a name applied to those consisting of small rounded grains resembling fish roe. Limestones also are named after the characteristic shells of which they are composed, such as coral, crinoid, and coquina. Travertine, a product of chemical precipitation from hot springs, is classed with limestones.

Limestones occur in every state, but only a relatively small number of the deposits are suitable for use as dimension stone or are favorably situated for quarrying or marketing. The well-known Indiana deposits furnish a large share of all sales.

Alabama—Alabama normally is an important producer of oölitic limestone but operations were suspended during the recent war. The largest development is near Rockwood, Franklin County, where a large mill is provided with the most modern equipment.

Florida—Shell limestones are quarried for building purposes in Volusia and Pinellas Counties.

Indiana—Indiana oölitic limestone is one of the most widely known building stones. This state produces 80 to 85 pct of all the building limestone sold in the United States. More than 20 companies operate 30 to 40 quarries and mills, and about a dozen more operate only finishing mills. The limestone used occurs in a massive bed 25 to nearly 100 ft thick, which extends north and south for a distance of about 125

miles. It is tilted gently westward with a dip of 34 to 70 ft per mile. It is of two principal colors, buff and gray. When first quarried it is comparatively soft and easy to work but it becomes harder upon exposure to the weather. Its workability is one of its principal assets. It is an attractive, durable stone that is used widely both for public buildings and in private construction. The chief centers of production are in the Bedford-Bloomington district in Lawrence and Monroe Counties. Some stone is quarried at St. Paul, Decatur County, and at Romona, Owen County.

Kentucky—Warren County was a prewar source of limestone similar to that produced in Indiana. The finishing mills were in Bowling Green.

Minnesota—Yellow and pink limestones quarried near Kasota, LeSueur County, were at one time popular as interior decorative stone but the quarries are now idle. Dolomitic limestone was quarried some years ago at Mankato, Blue Earth County, and Winona, Winona County, for heavy masonry, bridge construction and building purposes. Rough construction stone is quarried at Mendota, Dakota County, and Red Wing, Goodhue County.

Texas—A pale buff to cream oölitic limestone is quarried for building uses at Cedar Park, Williamson County. Other producing districts are Lueders, Jones County, and Butler, Travis County.

Colorado—Travertine that compared favorably with the Italian stone was quarried some years ago near Salida, Chaffee County. A green siliceous limestone is quarried at times near Manitou, El Paso County.

Other States—Limestone is quarried in a small way for building purposes in California, Illinois, Iowa, Kansas, Michigan, New York, Missouri, Ohio, Pennsylvania, Tennessee, Vermont, Virginia, Wisconsin, and Wyoming, and in Puerto Rico.

Quarry Methods for Limestone

Most limestone deposits used for dimension stone are nearly flat-lying and of limited thickness. Almost invariably the quarries are of the open-pit type. As the stone is worked out, the waste is thrown into the abandoned pits. Where usable beds are thin, much stripping may be required because the quarry must be widened constantly. If inferior stone lies over the good beds, it also must be removed, and sometimes the cost of removal is high. At some of the Indiana quarries, the overlying waste rocks form a continuous bed with the good stone. Blasting the waste rock, therefore, is impractical, as it would damage the good stone beneath. On this account, the waste rock is generally removed by channeling and wedging, which is expensive. Newsom³² has demonstrated that a horizontal cut may be made between the inferior and the marketable stone by means of a wire saw. At some quarries an open

seam separates the defective from the usable stone and the waste rock can be removed safely by blasting.

The first step in the process of block removal is channeling. The channeling machine is mounted on a frame and travels back and forth on a track. Steel bars operating with a chopping action similar to that of a reciprocating drill cut a narrow channel in the rock. Some are driven by steam and some by electricity. Channel cuts are made about 4 ft apart and 8 to 12 ft deep. The duplex machine, which makes a double cut, averages 200 to 300 sq ft of channel a day and the cost of cutting is 8¢ to 12¢ per square foot.

The high cost of channeling has encouraged operators to develop more economical methods. Wire saws have been tried successfully in several quarries. The wire saw consists of a three-strand steel cable of about $\frac{1}{4}$ -in. diameter. It runs as a belt and where it comes in contact with the rock it is fed with sand and water. It cuts rapidly, requires little power or attention, and reduces the waste greatly. It offers so many advantages that one would expect to find it in much wider use than it is at present.

When a floor is channeled, a key block is broken loose by driving wedges in the channel cut, and when it is removed space is provided for drilling beneath adjacent blocks. Wedges are driven in the drill holes to break the blocks free at the floor. When a wide floor space is obtained, successive masses of stone, each about 50 or 60 ft long, 4 ft wide and 12 ft high, are turned down on the quarry floor, where they are subdivided into mill blocks by driving wedges into small, shallow drill holes. Common mill block sizes are 10 by 4 by 3 ft and 10 by 4 by 4 ft. The blocks are hoisted from the quarry with steel or wooden derricks and are either piled in storage within reach of the derrick arm or are loaded on railroad cars and taken to a storage yard or to a mill for fabrication.

Preparation of Limestone for Market

Much limestone is sold as mill blocks and such blocks must have smooth faces and must be trimmed to true rectangular shape. The process of trimming blocks is known as "scabbling." Various methods of scabbling are employed; it may be done by hand with a scabbling pick, with circular saws, wire saws, heavy iron disks provided with cutting tools, diamond-toothed drag saws, or scabbling planers. The planers consist of massive blades, which scrape the surface. Such blades will remove $\frac{1}{4}$ to $\frac{1}{2}$ in. of stone at each cut. Blocks for export trade or for shipment to distant mills are scabbled most carefully.

Where blocks are fabricated into finished products in near-by mills the scabbling step may be omitted. Well-furnished finishing mills are equipped for drafting and patternmaking, sawing, planing, jointing, milling, turning, fluting, cutting, carving, packing, and shipping. Most

limestone fabricated in mills in the quarry districts is furnished on contract for specific jobs and therefore each block or slab is cut for its particular place. Consequently, the preparation of detailed shop drawings and patterns is an important preliminary step. A drawing of the block showing exact dimensions is consulted at each step in the manufacturing process.

Overhead traveling cranes with lifting capacity up to 50 tons handle blocks of stone expeditiously. Heavy, powerful cranes are used for large blocks and lighter, more rapidly moving cranes for smaller pieces.

The first step is to saw rough blocks into slabs. Gang saws like those described in the section on granite are used generally. They operate with a swinging motion, the blades lifting toward the end of the stroke and permitting the abrasive to wash under them. The abrasives used are sand, "chats" (cherty rock obtained at the Missouri lead and zinc mines), and steel shot. Limestone saws much faster than granite; the blades sink at an average rate of about 6 in. an hour. A straight blade with diamond teeth is used for making single cuts.

Circular diamond saws are used generally for making subsequent cuts. Common sizes are 60-in., having 84 diamond teeth, and 72-in., having 110 teeth. Each saw is designed for a standard speed and should be run at no other. With care, a saw may be used for six months to a year without conditioning. The cutting edge must be cooled constantly with a stream of water. The saw travels at a rate of 3 to 16 in. a minute, depending on the depth of the cut. Silicon carbide saws are used also.

A planer is a machine provided with a cutting tool having lateral and vertical adjustment. As the block of stone is carried beneath it on a traveling bed or platen, a thin layer of stone is scraped from the surface. Both sides and tops of blocks may be planed to desired dimensions. By using tools of any prescribed pattern, moldings may be cut. Some planers are adjusted to cut curved forms. A carborundum planer consists of two silicon carbide saws with a drum of smaller diameter between them. They trim both top and sides of the block with one motion.

Lathes similar to those used in machine shops are used for turning columns or balusters. Fluted columns are made by first turning the column to a true cylinder, then mounting a fluting tool on the tool post of the lathe. The tool travels back and forth while the column is held stationary. Carborundum wheels are used for fluting also.

A "milling machine" has a rotating cutting head with right-and-left and vertical worm-gear motions. With tools of various shapes and sizes, recesses may be cut and blocks of intricate design roughed out so nearly the desired shape that the hand carver's work is reduced substantially.

Carving requires more skill than any other limestone-cutting opera-

tion. Most of it is now done with pneumatic tools of many shapes and sizes. Patterns are used for the simpler shapes and plaster of paris models for the more complicated figures. Many beautiful churches, libraries and other public buildings attest the adaptability of architectural limestone to carving.

Building limestone is sold with various types of surface finish. A tooled surface has fine parallel grooves. A four-cut surface is made with a planer tool having four corrugations to the inch. A bush-hammered surface is rough and pitted. A shot-sawed or ripple surface is deeply scored by using steel-shot abrasive with gang saws. Chat-sawed is somewhat smoother than shot-sawed.

Railway cars are brought into the mill so that the mill hoisting equipment may be used for loading. All blocks are numbered and lettered to show their position in the structure and are packed carefully in excelsior and limestone dust in open-top cars.

Limestone Products

Some companies quarry only and sell the quarry product as rough blocks, or they may have sawmills and sell part of their output in the form of slabs. A second group of companies quarries limestone and manufactures it into finished products. Other companies have no quarries; they buy rough blocks or slabs and manufacture them into finished products. Although cut stone is the chief finished product, increasing quantities of a rougher type of building stone known as "sawed or broken ashlar" are now marketed. It is made in strips 3 or 4 in. thick and in units of different heights that will combine to give even-range levels. It is well adapted for stone veneer on residences.

Costs of Limestone

The following data on costs apply to the period immediately preceding the second World War.

Quarry costs range from 20¢ to 30¢ a cubic foot of block stone. The chief item is channeling, which ranges from 8¢ to 12¢ a cubic foot of recovered stone. Milling costs vary greatly, depending upon the amount of work done on each block of stone. Gang-sawing costs 35¢ to 45¢ a cubic foot of finished product. Subsequent sawing costs 12¢ to 15¢ more. Carving adds greatly to the cost. Paper work, including drafting, shop drawings, and patterns, may cost 15¢ to 20¢ a cubic foot on average jobs. The total cost of preparing building limestone with a moderate amount of carving ranges from \$1.50 to \$2.50 a cubic foot. Costs in 1946 were considerably higher.

SANDSTONE

With few exceptions, sandstones consist of quartz grains compacted and cemented together. The four commonest cementing materials are

iron oxides, clay, calcite, and quartz. The last is the most desirable but if very firmly cemented with quartz the rock becomes a quartzite, which is used little because it is too hard to be worked. Sandstones are sometimes named after their most abundant impurity; for instance, ferruginous, micaceous, calcareous, and argillaceous. They are sometimes named after their color, as brownstone. Bluestone, however, is a term applied to certain thin-bedded or easily cleavable sandstones irrespective of color. Bluestones are also termed flagstone and cleftstone. Freestone is a name applied to architectural sandstones that are cut or carved readily with no tendency to split.

The most important use of sandstone is for building purposes but it has a variety of other uses. Large quantities of curbing and many paving stones are made of sandstone. Flagging is produced for steps, sidewalks, and platforms. Grindstones, pulpstones, and other abrasive products are made in considerable quantities. Miscellaneous uses include slabs for grave vaults, laundry tubs, electrical switchboards, and lining for acid tanks. Sandstone blocks are used in the same way as silica brick for lining metallurgical furnaces. Quartzites are used as grinding pebbles and for lining tube and ball mills.

Following are the principal sandstone-producing areas.

Kansas—Rough building stone and flagging are produced near Redfield, Bourbon County.

Minnesota—Quartzite produced at Jasper, Rock County, is used for grinding pebbles and to line tube mills.

New York—An important paving-stone and curbing industry flourished at one time at Albion, Medina, and other points in Orleans County. The paving-block industry has virtually disappeared but considerable curbing is still manufactured. Bluestone of Devonian age is quarried in several places along the Hudson and Delaware Rivers. Flagging is an important product.

Ohio—Ohio produces about 60 pct of the total output of sandstone in the United States. Blue, gray, buff, and variegated sandstones of Carboniferous age cover a wide area extending from Portsmouth northward to Norwalk, and from there eastward to the northeastern corner of the state. The largest quarries that produce stone for building, curbing, flagging, rubble, and grindstones are near Amherst and other points in Lorain County. Many grindstones and pulpstones have been produced near Empire, Jefferson County, and at Constitution and Marietta, Washington County. Variegated architectural stone is obtained near Glenmont, Holmes County. Quarries are operated also in Harrison and Fairfield Counties.

Pennsylvania—There are no large sandstone quarry centers in Pennsylvania but small quarries are operated in several places. Building stones other than bluestone are produced chiefly in Chester and

Montgomery Counties. Bluestones similar to those in New York are quarried in Lycoming, Susquehanna, and Westmoreland Counties.

Tennessee—A widely used flagstone, also used for building purposes, known as Crab Orchard stone, is quarried in Cumberland County.

West Virginia—Grindstones and pulpstones are produced at times near Ravenswood, Jackson County, and at several places in Monongalia County. In the latter, building stone also is produced.

Wisconsin—Building stone is quarried in Clark County and to a smaller extent in Marathon, Portage and Wood Counties.

Other States—Sandstone is quarried in Fauquier County, Virginia; Pierce County, Washington; and at several points in California.

Quarry Methods for Sandstone

Quarry methods depend on rock structures and on the hardness of the stone. Moderately spaced joints in parallel systems are of great advantage. Quarry walls are maintained parallel with them. Most sandstones used for dimension stone are in nearly flat-lying beds. If open-bed seams are a few inches to 3 ft apart, the deposit is described as thin-bedded; if they are farther apart, it is thick-bedded; and if the rock is massive, showing no open-bed seams, it is said to be tight-bedded. The rift or direction of easiest splitting is almost always parallel with the bedding. A second, less pronounced direction of splitting, known as the run, is usually perpendicular to the rift. It is of great advantage in shaping paving blocks.

The greatest production of sandstone is of the softer types, which may be cut readily with channeling machines. As a rule, sandstones so hard that they make good paving blocks are too hard to channel, and primary breaks must be made by blasting.

The channeling process is much the same in sandstone as in limestone, except that the quartz grains wear the steel more rapidly. Steel must be changed frequently. Cuts are about 4 in. wide at the top but become much narrower because of loss of gauge through wear. A stream of water carries away the sand cuttings. Channel cuts are made parallel or at right angles to the major jointing systems. The large masses of sandstone separated by joints or channel cuts may be free at the quarry floor if bed seams are present. If not, a separation is made by driving wedges in drill holes. Subdivision of the larger masses is done by wedging supplemented at times by light charges of black blasting powder.

Bar and hammer drills like those described in the section on granite are used generally. The rate of drilling varies greatly, depending upon the hardness of the stone. In some Ohio quarries, where large grindstones and pulpstones are made, a circle-cutting drill is used. The drill is mounted on a rotating arm and cuts a circular channel.

Small charges of black blasting powder are used for blasting because heavy charges or high explosives would shatter and destroy the stone. The Knox system of blasting is often used. The drill hole is grooved with a flanged tool in line with the direction in which the split is to be made. A plug of cotton waste is placed some distance above the charge and the hole above the plug is filled with sand or other stemming. The air space permits the force of the charge to be exerted over a relatively wide area, which reduces the danger of local shattering. Sometimes air spaces are left both above and below the charge.

The usual plug-and-feather wedges are used for subdividing blocks. For bed-lifting, the wedges usually are driven into notches rather than into drill holes. In both blasting and wedging, the direction of the break should, if possible, follow the "run" of the rock.

Blocks usually are hoisted from quarries by derricks. The mass of rock worked out from one position of a derrick is called a "motion." The average area of a motion in Ohio is 134 by 61 ft. Grab hooks, chains, and cable slings are used for block attachment.

Preparation of Sandstone for Market

Manufacture of Paving Stones—Sandstones in which the grains are firmly cemented together with silica may be used for making paving stones. Paving blocks are shaped either on the quarry floor or in a near-by yard. The process is similar to that described in the section on granite. Directions of rift and run are followed carefully.

Mill Arrangement—Finishing mills for producing building stone, grindstones, curbing and other fabricated products are associated with many quarries. Modern mills are arranged and equipped to promote direct and speedy movement of material through the successive steps of manufacture. A distinctive feature of the better mills is the use of "transfer" and "gang" cars. A block for sawing is placed on a gang car. Transfer cars are run on a depressed track and have short sections of track across the top. A gang car with a load of finished slabs may be moved quickly from beneath the saws onto a transfer car and taken away, and another transfer car bearing a gang car with a new block may be conveyed immediately to a position in front of the gang saw. Thus a new block can be placed in position for sawing with very little delay.

Sawing—Gang saws similar to those used in granite and limestone mills are generally employed. Gangs with 10 to 15 blades saw average sandstone blocks 5 to 7 ft long at a rate of 3 to 8 in. an hour when sand is used as abrasive, and 6 to 12 in. an hour when steel shot is used. Subsequent sawing of slabs may be done with carborundum circular saws or with blades mounted with diamond teeth and set in straight-cut gang frames. Diamond circular saws have not proved satisfactory for

sawing sandstone. Wire saws are used in some places for jointing sandstone blocks.

Rubbing—A sand-rubbed surface finish usually is demanded. A rubbing bed consists of a heavy iron disk 10 or 12 ft across, which rotates in a horizontal plane. The block or slab of stone is held on the surface and when sand and water are supplied the block is ground smooth and reduced to proper dimensions.

Planing—Moldings are cut with planers, usually of the reversible-head type that cut in both directions. For hard sandstones, a stream of water must be directed onto the cutting edge to prevent burning of the tool.

Manufacture of Curbing—Curbing is an important sandstone product. The larger blocks usually are split to slabs of the approximate dimensions desired, although massive rock with no pronounced rift may be sawed to size. Curbing mills are equipped with planers and overhead cranes or pneumatic hoists. Rough blocks are brought into the mill on flat cars, are planed, then reloaded on the same car.

Manufacture of Grindstones and Pulpstones—The stones are cut in circular form in the quarry by means of the circle-cutting drill described previously, or rectangular blocks may be scabbled to circular form. They are then mounted on axles and trimmed to final form with steel bars held against the surface while the stone is rotated.

Cutting and Carving—Building stone is shaped with pneumatic tools and columns are turned in the same manner as in limestone-finishing mills.

The Bluestone Industry—The characteristic "cleftstone" occurring along the Delaware, Hudson, and Susquehanna Rivers is usually worked in relatively small quarries and hauled to central shipping points known locally as docks, situated on navigable water or railway lines. Some of the stone splits with remarkable ease into slabs that may be 10 or 12 ft square and only 2 in. thick. It was widely used for sidewalks and steps before concrete came into general use. Edge stone, which splits in thicker beds, is used for curbing, sills, caps, and coping. What is known as "rock" is taken from the more massive beds and is used for building stone.

Waste Utilization—Waste sandstone in large irregular blocks is used as riprap for shore protection, harbor work, or spillways at dams. Waste may be crushed for road stone and concrete aggregate. Sand is an important by-product that is used for manufacture of sand-lime brick, for mortar and plaster, for furnace use, or as engine sand.

MARBLE

Marbles may be classed in three groups. The largest comprises those derived from limestone by recrystallization resulting from the heat and pressure of mountain-building forces. Exceptionally, the re-

crystallization seems to have been brought about chiefly by circulating water, for there may be no evidence of extreme pressure or deformation of the beds. Such marbles may be either high-calcium or dolomitic. The second group comprises the onyx marbles, also called Mexican onyx and cave onyx. They are chemical precipitates of calcium carbonate from cold-water calcareous springs. Usually they show highly ornamental banding. The third group consists of the verd antique or serpentine marbles. They may contain little calcium carbonate but they take a good polish and are used in the same way as are the true marbles. Green is their prevailing color. They may be streaked with white or red and may show ornate patterns.

The principal use of marble is as building stone for both interiors and exteriors. For exterior use, marbles must be enduring and free of impurities that may stain or corrode the surface. For interior use, including floor tile, stair treads, balusters, baseboards and columns, decorative effects are most important. Marble is used also for memorials, statuary and novelties. Onyx marble is particularly adapted for the latter.

As marble results primarily from regional metamorphism, the most important deposits occur in the Appalachian Mountains of the eastern states and in the Rocky Mountain and coast ranges of the west. Marbles that occur sparingly in the central states have been recrystallized by processes involving little or no deformation of the beds. The four leading states in order of production value in 1946 were Vermont, Georgia, Tennessee and Alabama.

Alabama—A bed of marble at least 200 ft thick occurs near Sylacauga, Talladega County. It is fine grained and mostly white. Some beds are of statuary grade; in other beds, layers of light green talc and other silicate minerals give ornamental patterns. The rock is exceptionally pure, running 98 to more than 99 pct calcium carbonate, and is of very low porosity. It is used for exterior and interior building and decoration and for monuments. The marble is fabricated in well-equipped mills.

Arkansas—Gray marble is quarried for building and monumental uses near Batesville, Independence County.

Georgia—Georgia is an important producer of building and monumental marble. The industry is confined almost entirely to the vicinity of Tate and Marble Hill, Pickens County. Highly crystalline white, gray, bluish, and pink marbles are produced in several wide and deep quarries and are fabricated in large, well-equipped mills. Most of the Georgia marbles are coarser grained than either the Alabama or the Vermont marbles.

Maryland—An ornamental verd antique marble is quarried at Cardiff, Harford County.

Missouri—Light gray marbles are quarried at Carthage, Jasper

County, and Walnut Grove, Green County. A small marble output is recorded from Ste. Genevieve County.

Tennessee—The Tennessee marbles occur in the Holston member of the Chickamauga formation of Paleozoic age. They lie in the valley of the Tennessee River in the vicinity of Knoxville. Seven parallel belts of commercial marble are recognized; namely, Luttrell, Black Oak, Concord, Knoxville, French Broad, Meadow, and Bays Mountain. Many quarries produce light pink and gray marbles used principally for floors, steps, wainscoting, sanitary enclosures, and other interior structural and decorative uses. The stone is used less extensively for exteriors but a notable exception is the exterior of the National Gallery of Art in Washington, D. C. Tennessee marble is characterized by irregular or zigzag gray, black, greenish, or reddish markings known technically as stylolites but more generally as "crowfoot." Unlike most marbles, those of Tennessee are fossiliferous. Large, well-equipped finishing mills are operated in conjunction with the quarries and much material is shipped also in rough block form to finishing mills in other states.

Vermont—A great marble belt about 80 miles long lies in western Vermont between the Green Mountains and the parallel Taconic Range to the west. The beds are highly folded and produce complex structures that make quarrying difficult. The workable beds have a total thickness of several hundred feet. Marbles in many colors, including white, cream, gray, variegated, green, and blue, are used for exterior and interior building and decoration and for monuments. Large quarries are operated at various points in Rutland County. Black marble is obtained at Isle La Motte, Grand Isle County, and verd antique at Roxbury, Washington County. Large sawing and finishing mills are maintained.

Other States—Marble was obtained at one period from tidewater quarries at Token and other points in Alaska. Onyx marbles are quarried sporadically in a small way in Arizona. Marbles of many kinds occur at various points in California but there has been little recent activity. Pink and buff building marbles are quarried at Kasota, Le Sueur County, Minnesota, blue and gray marbles at Marble, Cherokee County, North Carolina, and building marble in Tooele County, Utah. Terrazzo and other marble by-products are produced in Tuolumne County, California, near Canon City, Freemont County, Colorado, and in several other states.

Quarry Methods for Marble

Marble beds usually are tilted and folded, and as they vary in thickness and position from point to point, thorough prospecting is required and development must be planned carefully. Both open-pit quarries

and underground mines are worked. The most difficult step in underground work is driving the preliminary tunnel or heading. Blasting methods may be used but channel cuts at the floor are essential to prevent the blasts from shattering the marble beds. If the heading is in good marble, ceiling and floor cuts may be made with channeling machines and vertical cuts with a drill mounted on a swivel, a machine known as a Radiolax. Although such cutting processes are slow, marble thus removed is preserved for commercial use. After the heading has been advanced, underground operations are similar to those in open quarries except that pillars must be left at intervals to support the roof.

Primary cuts generally are made with channeling machines, which have been described in preceding sections. A favorite machine is the double-swivel channeler, which may be used for both vertical and inclined cuts. Electric air machines are in common use. The rate of channeling varies greatly; recorded averages range from 25 to 80 sq ft a day for one machine. The quarry floor may be enlarged by inclining channel cuts outward. This process is known as undercutting.

Wire saws have been tried at several places and some degree of success has been attained in Arkansas and Vermont. The wire cuts slowly and wears out more rapidly than in slate or limestone. Further tests are contemplated.

The larger masses are separated from the quarry floor and are subdivided by drilling and wedging. The rift (direction of easiest splitting) usually follows the bedding but commonly it is not well defined, therefore to secure straight breaks holes must be drilled almost the full depth of the blocks and only a few inches apart. Long wedges are used and some of them are designed to exert pressure throughout the full length of the drill hole rather than at a single point.

Hoisting usually is done with powerful derricks that may have lifting capacities of 15 to 18 tons. The hoist cable may be attached to the marble block by grab hooks, chains, or cable slings.

If marble blocks are to be shipped some distance, they are usually "scabbled"; that is, trimmed to true rectangular shape. It may be done by hand with a scabbling pick, by slabbing off the irregular masses with wedges in drill holes, or by cutting with a wire saw.

Preparation of Marble for Market

The term "mill" usually is applied to the part of the finishing plant where blocks are sawed into slabs; all other manufacturing processes are classed as shop work. The mill and shop usually are so close together that both may be served by the same overhead traveling crane, although small and large cranes may be operated on the same tracks.

Modern marble mills are equipped with transfer and gang cars as described in the section on sandstone. Gang saws like those used in

limestone mills are in general use. Marble saws slowly. In stone of moderate hardness the blades may sink at a rate of 1 to 2 in. an hour; in the harder, siliceous marbles, they may sink not more than 3 or 4 in. during an entire shift. Some large marble mills are equipped with more than 40 gang saws.

When slabs of marble enter the shop, the first processes of manufacture are known as coping and jointing. The former is the process of cutting one slab into two without regard to the finish of the edges. Jointing is the process of cutting true to specified sizes and shapes and with smooth, unchipped edges. Carborundum machines generally are employed for this work.

Slabs or blocks may be squared and finished on rubbing beds like those described in the section on sandstone. Irregular surfaces are rubbed by hand with abrasive bricks or with pieces of marble supplied with sand and water.

Gritting, a process that gives a smoother surface than rubbing, is accomplished usually with abrasive bricks attached to revolving buffer heads. The bricks may be of silicon carbide or aluminum oxide. Gritting produces what is known as a "hone" finish. Buffing, the process that gives a fine polish to the marble surface, is done with wet "putty powder" (tin oxide) carried on a revolving felt buffer head.

Recutting of blocks and slabs in the shop may be done with circular diamond saws, perforated steel saws using steel shot as abrasive, or with a straight blade in a gang frame. Diamond saws are used most widely. Moldings and cornices are cut with planers (described under Preparation of Limestone).

Carborundum machines are used widely for cutting moldings, balusters, and fluted columns. Columns may be cut with rotating drums fed with steel shot but generally they are roughed out by hand and then turned in a lathe. The column is first turned to size with a cutting tool, as in ordinary machine lathe work, ground to a smooth surface with abrasive powders, and polished with putty powder.

Cutting and carving are done principally with pneumatic tools supplemented by sandblast processes, as described in the section on granite.

Waste Utilization—Waste marble blocks may be used as riprap or for rough construction stone or they may be crushed for road stone and concrete aggregate. Usually marble is low in impurities and so may be used for manufacturing lime or for chemical applications. It may be ground for agricultural use or as filler, or may be pulverized to extreme fineness for "marble floor," which is used as whiting.

SOAPSTONE

Soapstone, as the term was used originally, apparently was synonymous with steatite or massive talc. The term as now used relates to all

dark gray to greenish talcose massive rocks. Soapstones are metamorphic rocks, generally containing 10 to 80 pct talc, and the remainder chlorite, amphibole, pyroxene, mica, calcite, dolomite and other minerals.

Soapstone was first used in the United States by the American Indians, who shaped it into bowls, pots, cooking stones, and other objects now seen in many museums. Although a small production has been noted at various times in Maryland, North Carolina, Rhode Island, Vermont, California, and Washington, Virginia has always dominated the industry. An extensive deposit in Albemarle, Nelson, and Orange Counties was first developed about 1880. The largest operations are conducted near Schuyler.

The Virginia deposits are regarded as alteration products of basic igneous rocks high in magnesium. They occur as irregular or lenslike dikes 100 to 200 ft wide, bordered with mica schist and peridotite.

The quarries are 100 ft or more long, 100 to 120 ft wide, and are worked to a depth of about 200 ft. No explosives are used. Cuts are made with channeling machines and, after removal of a row of key blocks, all other channeled masses are undercut to their full depth. The long masses thus set free are subdivided by drilling and wedging in the direction of the natural grain. As the grain dips at angles of 30° to 60° , the blocks are roughly diamond-shaped. Average blocks are 4 by 4 by 6 ft.

Milling processes are similar to those in marble mills. Slabs cut with gang saws are trimmed with steel-toothed hand saws similar to those used in wood working. Slab surfaces are smoothed on rubbing beds and are tongued and grooved with carborundum machines before assembling as laundry tubs, sinks, acid tanks, aquariums, and similar products. An important branch of the industry is the manufacture of furnace blocks to line retorts in paper mills. Soapstone is used extensively in building construction for wainscoting, sills, caps and spandrels. The harder varieties are used for floor tile and stair treads.

On account of its resistance to chemicals, soapstone is used in the manufacture of laboratory hoods, sinks, and tables, photographic laboratory tanks, and similar equipment. It is used for switchboards and other electrical insulation units also. Because of its ability to resist and retain heat, it is employed for griddles, footwarmers, and fireless-cooker stones; but these uses are declining.

GREENSTONE

A metamorphic rock related in origin to soapstone but consisting essentially of actinolite and chlorite is quarried at Lynchburg, Virginia. Because of its characteristic color, it is called greenstone. It has an attractive, unfading color, which makes it popular for ornamental building purposes. It has nonskid qualities that recommend it for floor tile

and steps. It is used also for making furnace blocks and has been employed with some success as a constituent of refractory brick.

MISCELLANEOUS STONE AND BOULDERS

Basalt, gabbro, and other basic igneous rocks are used to some extent for building purposes. Tuffs, rhyolites, and other porous volcanic rocks, are used sparingly as light-weight building materials. Mica schists are used as abrasive stones, for lining kilns and furnaces, and also for building purposes. Diatomite, tripoli, and pumice are shaped into refractory or filter blocks.

Boulders are "rolling stones," masses of rock loosened from the parent ledge by natural processes. Usually they are plentiful where the bedrock is close to the surface. In the unglaciated regions of southern United States, boulders generally have not been transported far; therefore, in limestone regions they consist of fragments of the underlying limestone and in granite regions they are of granite. In New England and other northern glaciated territory, however, the ice sheet may have carried them for many miles, and in any locality may be found boulders of granite, limestones, sandstones or conglomerates assembled from widely scattered sources.

Boulders were used by the most ancient races for building primitive dwellings and they are still important construction materials. Local boulders are used extensively in building rustic fireplaces, chimneys, basements, or entire houses. Many large mansions, clubhouses and mountain resorts are made of them. As they are obtained locally and are not a product of the quarry industry, we have no record of the extent of their use. They are used in making fences and retaining walls. Where boulders are abundant, many miles of stone fences are a characteristic feature of the countryside.

ENDURANCE OF BUILDING STONE

Stone is one of the most enduring of all building materials. In the Old World, many stone structures built 500 to 1000 years ago are still in good condition. There is great variation in the endurance of stones, however, and some of them decay comparatively rapidly. The conditions of outcrops that have been exposed for countless years are the best evidence as to resistance to weathering, though observations made on stone buildings are helpful; but in America few of our structures are more than 200 years old and most of them have stood for less than 100 years.

Tests of the enduring qualities of stone are now made in laboratories. By repeated freezing and thawing of wet samples, the results of exposure for many winters and summers may be shown within a few weeks. Most commercial stones have been tested thoroughly and no reliable quarry-

man will recommend for exterior use any stone that will not pass the most rigid tests for endurance.

The question often is raised as to which kind of stone is the most enduring. A general answer cannot be given because one kind of stone may be susceptible to certain agencies of decay and quite resistant to other disintegrating forces. The carbonate rocks (limestones and marbles) are altered chiefly by chemical action and to a much smaller degree by physical agencies. The granites, syenites, and other igneous rocks, on the other hand, suffer most from physical agencies such as repeated expansion and contraction as a result of sudden and excessive changes in temperature. Sandstones with calcareous cement are affected in much the same way as limestones and marbles. Firmly cemented siliceous sandstones are very enduring. Slates are affected very little by solution, expansion or contraction, but a high calcium content may lead to rapid disintegration if the slates are exposed to acid fumes or solutions. Thus it may be seen that a marble or limestone might be less enduring than a granite in an acid atmosphere, and a granite might disintegrate more rapidly than a marble or limestone under extreme temperature changes. Even under adverse conditions, however, deterioration is an extremely slow process and any standard stone produced by reliable operators is so enduring that the question of permanence need scarcely be given attention.

The permanence of stone masonry depends not only upon the quality of the stone itself but upon quality of supplementary materials and workmanship. Roofs, gutters, flashings, and window casements should be so constructed that water cannot run behind stone facing blocks. Masonry mortars of only the highest quality should be used. All bedded stones should invariably be placed in the wall with the bedding plane horizontal.

TESTS, SPECIFICATIONS AND MARKETING

The stone of no two quarries is exactly alike. To take advantage of this individuality in stone, architects and builders desire the utmost freedom in selection. Therefore specifications relate chiefly to workmanship and surface finish and little is said about color, texture or general appearances. The American Association of State Highway Officials, however, has issued specifications for ashlar and rubble to be used in bridges and incidental structures. They relate chiefly to soundness, durability, and absence of seams, cracks or other defects.

Although few general specifications are in use, individual contracts may call for exacting requirements to satisfy special conditions. Thus, a patterned floor requires tile of different colors and it is essential that they should not differ greatly in resistance to abrasion. Stone for sanitary uses should have a very low ratio of absorption. Stone for labora-

tory use should be resistant to chemical action. These special requirements call for a great deal of testing and many results of tests have been published.^{21-24,29,36}

The simplest method of marketing dimension stone is to sell rough blocks directly to dealers or manufacturers, and a number of producers do this. Some have mills where they saw the blocks, and such producers may sell either slabs or rough blocks to dealers or manufacturers. Most of the large companies that produce structural stone have their own finishing mills. They take contracts for individual structures and fabricate according to specifications. Most monumental granite is sold in rough blocks to manufacturers of memorials, although some important quarrying units also manufacture. A large proportion of monumental marble is manufactured by the producing companies and is sold to the retail monument trade. Paving stones and curbing are sold to contractors, municipalities, or dealers.

FOREIGN TRADE

Building and ornamental stones are imported into the United States in considerable quantities. Most of the imports under normal trade conditions are marbles from Italy, Spain, France, Belgium, Portugal, and England. Granite, chiefly for memorials, is imported from Finland, Sweden, and Canada. Travertine imports from the well-known deposits at Tivoli, near Rome, attain considerable magnitude at times. Onyx marble, of which there is very small production in the United States, is obtained from Lower California, Mexico, and the Province of San Luis, Argentina.

Exports of marble are much smaller than imports. Granite, limestone, and sandstone exports are not classified separately and therefore cannot be determined exactly, but they are very small. Canada is the chief consumer.

The U. S. Tariff Act of 1930 provided for an import duty of 60 pct ad valorem on manufactured and 25¢ per cubic foot on unmanufactured granite. The duty on marble and onyx in rough blocks was 65¢ a cubic foot and on sawed and dressed over 2 in. thick, \$1 per cubic foot. Smaller sizes carried a duty of 8¢ to 13¢ a superficial foot, with an additional charge of 3¢ if rubbed and 6¢ if polished. Manufactured articles chiefly or entirely of marble carried a duty of 50 pct ad valorem. On unmanufactured sandstone and limestone, the duty was 15¢ per cubic foot, and on hewn, dressed, or otherwise manufactured stone, 50 pct ad valorem. Unmanufactured travertine carried a duty of 25¢ a cubic foot.

The rates established by the Tariff Act of 1930 have been modified considerably by trade agreements. By virtue of a trade agreement with Sweden dated Aug. 5, 1935, the duty on granite paving blocks was re-

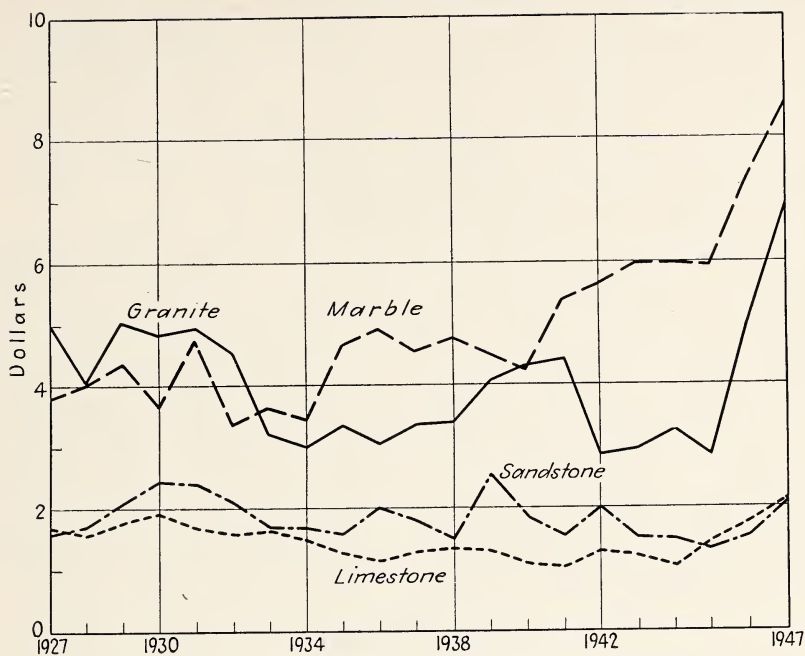


FIG 3—VALUE PER CUBIC FOOT OF BUILDING STONE, 1927-1947.

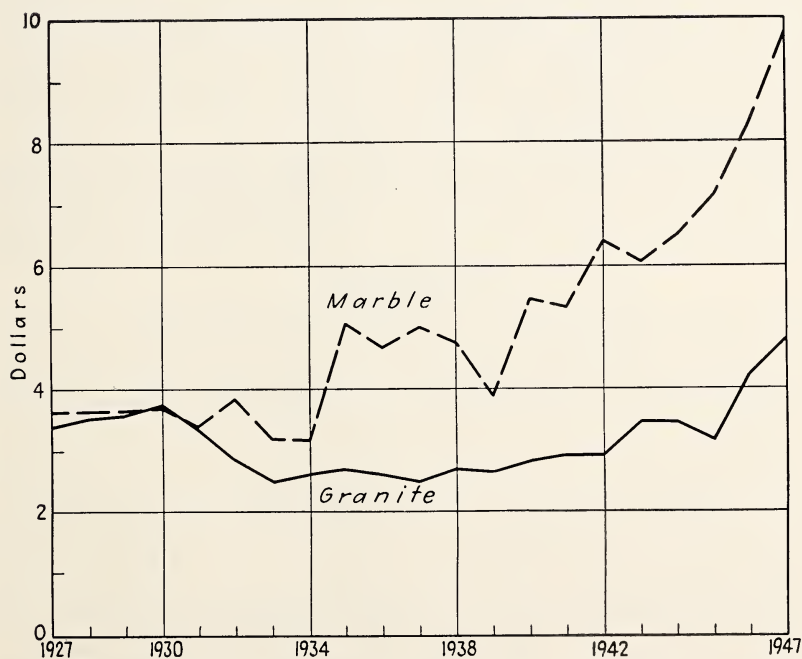


FIG 4—AVERAGE VALUE PER CUBIC FOOT OF MONUMENTAL GRANITE AND MARBLE, 1927-1947.

duced from 60 pct to 40 pct ad valorem. A Finnish agreement dated Nov. 2, 1936, reduced the duty on all granite hewn or dressed from 60 to 30 pct ad valorem. This had the effect of automatically reducing the tariff on paving blocks from Sweden from 40 pct to 30 pct. The duty on unmanufactured granite, which had been reduced from 25 to 20¢ a cubic foot under the Swedish trade agreement, was again reduced to 12½¢ under the Finnish agreement.

An agreement with France effective Jan. 1, 1948, reduced the duty on manufactured marble from 50 to 25 pct ad valorem. Black marble, nearly all of which is obtained from Belgium, was placed in a separate category, and, effective Jan. 1, 1948, the duty on rough blocks was reduced from 65 to 32½¢ a cubic foot, and on sawed and dressed from \$1 to 50¢ a cubic foot. Onyx marble was accorded a special classification, and, according to a trade agreement with Argentina dated Nov. 15, 1941, the duty upon it was reduced from 65 to 32½¢ a cubic foot. The new rate was applied to onyx from Mexico on Jan. 30, 1943.

The duty on unmanufactured sandstone and limestone suitable for use as monumental or building stone was reduced from 15 to 10¢ a cubic foot, effective Jan. 1, 1948.

PRICE HISTORY

Fig 3 shows the average selling price of each of the major types of building stone from 1927 to 1947. The materials included are cut, sawed, and finished building stone only and the unit values are determined from quantities sold and the amount received f.o.b. mill as reported to the United States Bureau of Mines. The unit value of marble was relatively high from 1941 to 1946.

Fig 4, based on statistics of the United States Bureau of Mines, shows trends in prices of monumental granite and marble for the same period. The upward trend in prices since 1941 is particularly noteworthy.

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CHAPTER 15
FELDSPAR
BY B. C. BURGESS*

IN the first edition of this volume,⁴⁴ feldspar was introduced as “the commonest mineral of the crystalline rocks,” usually in small grains associated with other minerals and commercially produced only from pegmatites. Now other crystalline rocks, such as alaskites and granites, have become present or potential sources of feldspar. In addition, feldspar has encountered very vigorous competition from such substitutes as nepheline syenite and aplite.

COMPOSITION AND PROPERTIES

The feldspars form a group of which the principal species are orthoclase, microcline, albite, and anorthite. These are aluminum silicates of potassium, sodium and calcium. There are also a barium feldspar, celsian, and barium orthoclase feldspar, hyalophane, rarely found and of no commercial importance. None of the minerals in the feldspar group are found pure or nearly pure. The potash feldspars, orthoclase and microcline, nearly always contain some albite (soda microcline, anorthoclase); the soda feldspars usually contain some anorthite (lime feldspar). There is a series of soda-lime feldspars known as plagioclase in which the albite and anorthite molecules replace each other in varying proportions from albite through oligoclase, andesine, labradorite, and bytownite to anorthite. Theoretical chemical composition of the principal feldspars is given in Table 1.

The Whiteware Division of the American Ceramic Society submitted a list of definitions of ceramic terms, in April 1947, for use in technical literature. For feldspar it gives: “A group of igneous minerals consisting chiefly of the aluminum silicates of potash, soda and lime, in which one base generally predominates.”

Commercial feldspars are intergrowths of at least two species of feldspar, which occur associated with one or more accessory minerals such as quartz, muscovite, biotite, garnet and tourmaline as well as with small but varying proportions of the decomposition product, kaolinite. An intergrowth of quartz and feldspar frequently contains

* Consulting Engineer, Monticello, Georgia.

about 75 pct feldspar and 25 pct quartz. The quartz often is distributed through the feldspar uniformly in wedge-shaped grains. This is referred to in the literature as "graphic granite" or "schriftgranit," and by the miners is called "corduroy."

Perthite is a feldspar of high potash-soda ratio, which exhibits a lamellar intergrowth of microcline and albite. Cornwall stone is a feldspar-quartz-kaolin product obtained from weathered alaskite-type granite in Cornwall, England. Carolina stone is a similar product made by chemically controlled blending in North Carolina. Both of these "stones" contain a little fluorspar. Most of the commercial potash feldspar produced and used is "perthitic" rather than straight microcline.

TABLE 1—*Composition and Properties of Principal Feldspars*

Constituent	Orthoclase (KAlSi_3O_8)	Microcline (KAlSi_3O_8)	Albite ($\text{NaAlSi}_3\text{O}_8$)	Anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$)
Chemical Composition, Theoretical Percentage				
SiO_2	64.7	64.7	68.7	43.2
Al_2O_3	18.4	18.4	19.5	36.7
CaO				20.1
K_2O	16.9	16.9		
Na_2O			11.8	
Physical Properties				
Crystal system.....	Monoclinic	Triclinic	Triclinic	Triclinic
Refractive index.....	1.524	1.526	1.529	1.584
Specific gravity.....	2.56	2.56	2.605	2.765
Melting point, deg C.....	1200	1200	1110	1532

The crystals of the different species are similar in angle, in general habit (Table 1), and in mode of twinning. The prismatic angles are nearly 60° and 120° . The cleavage is good in two directions at 90° , or nearly 90° . The luster is vitreous to pearly (subvitreous to dull in altered varieties). The streak is white. The fracture is uneven. Colors are generally white, cream and pink, also milky, buff, brown, red, gray, green and bluish. Hardness is 6 to 6.5.

ORIGIN AND MODE OF OCCURRENCE

According to Clarke,²⁶ the feldspars constitute 59.5 pct of the igneous rocks, quartz being the next most abundant single mineral at 12 pct. The hornblende-pyroxene (ferromagnesian) group comprises 16.8 pct of the average.

Pegmatites, the chief source of feldspar, vary greatly in mineral composition, but as the source of commercial feldspar, the "granite" type, consisting essentially of feldspar, quartz and mica, predominates,

Pegmatites are emanations from granitic magmas that have solidified in dike-like bodies in the enclosing rocks. Their formation probably has been a long-continuing process in which hydrothermal replacement followed the original magmatic injection. They are usually found in schists, gneisses, granite, diorite and other crystalline rocks. However, a few pegmatites are found in limestone and other sedimentary rocks. As a natural consequence of such a mode of origin, pegmatites are characterized by extreme irregularity in size and shape of the deposits, size and distribution of the essential minerals, and variety and proportion of the accessory minerals. According to Schaller,⁷⁷ the general paragenetic sequence in pegmatites is as follows: High-temperature potassium feldspar, inversion to microcline, a little perthite, quartz, albite, muscovite, and the general group of such minerals as black tourmaline, garnet and beryl, sometimes followed by lithium minerals, phosphates, sulphides, carbonates and oxides.

Alaskite is the name commonly applied to the pegmatitic granite formations in western North Carolina. Alaskite varies greatly in texture from the fineness of granite to the coarseness of pegmatite. The mineral composition continues fairly uniform, consisting of oligoclase, quartz, microcline, and muscovite in that order of abundance. Small amounts of garnet and biotite occur, especially near the contacts. Analysis 7, Table 2, is typical of the alaskites near Spruce Pine and Kona, North Carolina. Analysis 8 is of flotation concentrates from rock approximating analysis 7.

The kaolin content of all commercial feldspars is a result of the natural processes of rock decomposition. Surface weathering undoubtedly is the cause of kaolinization of the feldspars of the Southern Appalachian region of the United States. The kaolin in Cornwall stone may be the result of pneumatolytic action. Carbonic and humic acids are known to be effective agents in the surface kaolinization of feldspar. Sericitization often accompanies hydrothermal kaolinization. Either is often accompanied by solution of iron-bearing minerals, resulting in staining of the feldspar. Another deleterious impurity is manganese oxide, which frequently is found as dendrites on the cleavage planes of partially kaolinized feldspar.

DISTRIBUTION OF DEPOSITS

Pegmatites and alaskites that are present or potential sources of feldspar are found throughout the Appalachian region of the United States from Alabama to New York and also in the New England states. Minnesota was a producer for a few years. Now South Dakota and Colorado are large producers. California and Arizona supply the requirement of Pacific Coast industry. Wyoming recently has become a

TABLE 2—*Analyses and Calculated Mineral Content of Commercial Feldspars of the United States and Canada*

PERCENTAGES														
No.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	Loss	Potash Feldspar	Soda Feldspar	Lime Feldspar	Quartz	Other Minerals	Source
1	67.5	18.3	0.05	0.5	tr	10.3	3.0	0.3	61.0	25.4	2.5	8.0	3.1	North Carolina
2	68.8	17.8	0.1	0.5	tr	9.5	3.0	0.3	56.3	25.4	3.5	11.2	4.6	
3	69.5	17.5	0.1	0.8	tr	8.1	3.6	0.3	47.9	30.6	4.0	14.1	3.4	
4	73.5	15.3	0.1	0.5	tr	7.3	3.0	0.3	43.2	25.4	2.5	25.2	3.7	
5	69.0	18.2	0.1	1.3	tr	5.5	5.5	0.3	32.4	46.6	6.5	13.2	1.3	
6	70.0	18.1	0.1	1.5	tr	3.5	6.5	0.3	20.7	55.2	7.5	15.7	0.9	
7	74.6	14.9	0.2	1.2		3.9	4.6	0.3	23.0	38.5	6.0	30.1	2.4	Virginia
8	67.6	19.5	0.06	1.5		5.0	6.0	0.3	29.5	50.5	7.5	10.6	1.9	
9	67.3	18.5	0.05	0.5	tr	11.0	2.6	0.3	65.1	22.0	2.5	7.1	3.3	
10	69.1	17.5	0.1	1.0	tr	9.0	3.2	0.2	53.3	27.2	5.0	12.8	1.7	New York
11	68.1	20.1	0.1	4.0		2.5	4.9	0.3	15.0	41.0	19.7	21.2	3.1	
12	74.6	15.3	0.13	1.0	tr	2.8	5.8	0.3	16.6	49.3	5.0	26.7	2.4	New England
13	67.8	18.4	0.1	0.3	tr	10.0	3.0	0.3	59.2	25.4	1.5	8.8	5.1	
14	71.3	16.1	0.1	0.2	tr	9.4	2.9	0.2	55.6	24.6	1.0	17.0	1.8	Canada
15	74.0	14.8	0.1	0.3	tr	8.1	2.6	0.2	47.9	22.0	1.5	25.8	2.8	
16	65.5	18.7	0.1	0.4	tr	12.8	2.3	0.2	75.7	19.5	2.0	1.2	1.6	S. Dakota
17	65.7	19.6	0.1	0.7	tr	10.6	2.9	0.3	62.7	24.6	3.5	4.0	5.2	
18	64.7	19.7	0.04	0.3	tr	10.0	2.8	0.4	72.2	23.8	1.5	0.0	2.5	Colorado
19	66.3	19.4	0.13	0.7	tr	9.5	3.6	0.3	56.3	30.6	3.5	5.1	4.5	Arizona
20	65.1	19.7	0.04	0.3	tr	12.2	2.4	0.3	72.2	20.4	1.5	1.3	4.6	California
21	66.1	19.2	0.1	0.4	0.2	10.7	3.3	0.2	63.4	28.0	2.0	3.3	3.3	Georgia
22	73.8	14.9	0.1	0.2		9.2	1.9	0.2	54.4	16.0	1.0	27.3	1.3	
23	65.0	19.5	0.05	0.2		13.1	2.1	0.3	77.5	17.5	1.0	2.5	1.5	

producer of crude feldspar. Deposits are known in other western states from Texas to Idaho.

Analyses of commercial feldspars of the United States and Canada are given in Table 2. Scale of production of crude feldspar by states is shown in Fig 1 and data are listed in Table 3.

Pegmatites containing commercial feldspar are found in the provinces of Canada from Nova Scotia and Labrador to Manitoba, and through the Rocky Mountain area. The major portion of Ontario and most of the province of Quebec north of the St. Lawrence consist of crystalline rocks containing many pegmatite dikes.

The Scandinavian peninsula has long been the source of most of the feldspar used by European potteries. Andersen³ reports the examination of specimens of feldspar from upward of three hundred localities, for the most part situated in southern Norway.

Pegmatite dikes from which feldspar is, or may be, obtained are found also in Czechoslovakia, Germany, France, Italy, Rumania, Russia, China, Finland, India, Japan, Australia, Egypt, South Africa, Brazil and Argentina.

With the possible exception of a few dikes in Scotland,⁵⁰ no pegmatites that will serve as commercial sources of feldspar are known in

the British Isles, but in Cornwall, near St. Austell, large bodies of semikaolinized granite or alaskite are found, from which the product known as Cornwall stone or "china stone" is obtained. A somewhat similar formation is mined at St. Yrieix, France, southwest of Limoges. What would be considered in America a very low-grade pegmatite is mined in Germany for some of the feldspathic material used in that country.³⁹

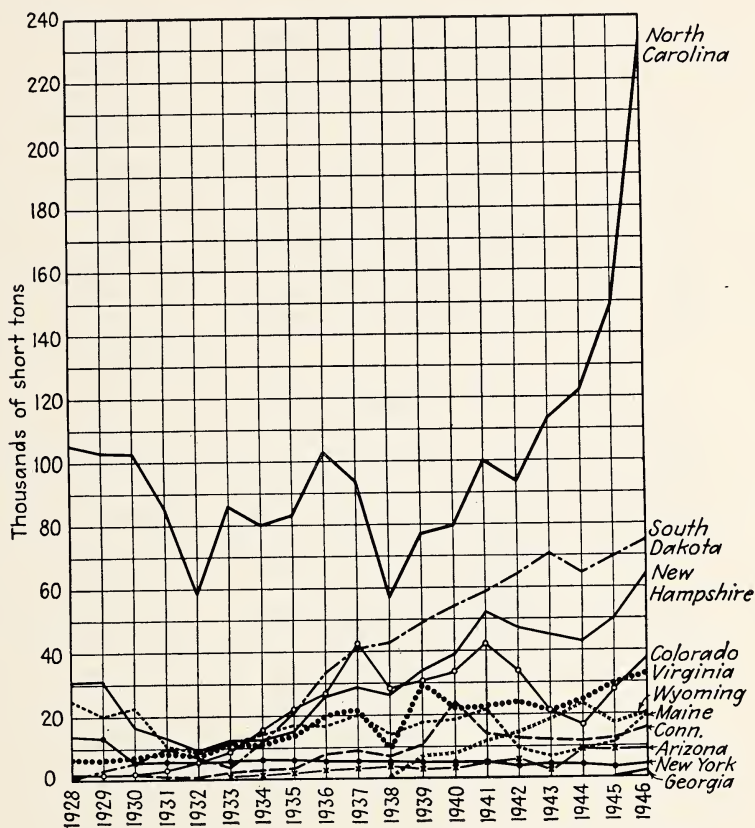


FIG 1—PRODUCTION OF CRUDE FELDSPAR IN THE UNITED STATES.

POLITICAL AND COMMERCIAL CONTROL

Owing to the wide distribution of deposits over the world and the comparatively low unit value of the product, feldspar has never entered largely into world commerce. The first porcelain products in which feldspar was used for its fluxing action, and for which it is principally used today, were no doubt made from "natural" pottery clays containing the requisite feldspar content. During the Ting dynasty (A.D. 621-945) there is evidence of the first use of feldspar as a separate material for manufacture of vitrified products in China, but it

TABLE 3—*Production of Crude Feldspar in the United States, 1928-1946*
LONG TONS (2240 LB)

State	1928	1929	1930	1931	1932	1933	1934	1935	1936	1937	1938	1939	1940	1941	1942	1943	1944	1945	1946
Arizona.....					1,232	2,000 ^a	2,000 ^a	3,000 ^a	a	a	4,000 ^a	3,200 ^a	3,700 ^a	5,000 ^a	6,000 ^a	3,000 ^a	9,800	8,800	8,700
California.....	11,891	12,770	6,519	4,465	2,000 ^a	1,433	2,000 ^a	3,015	4,700	1,836	1,396	2,076	2,711	4,464	5,090	2,000 ^a	1,200	800	
Colorado.....	2,000 ^a	2,000 ^a	1,933	2,953	5,612	8,000 ^a	10,000 ^a	22,275	25,806	42,221	27,452	2,995	34,105	42,326	33,610	20,659	15,787	26,279	37,312
Connecticut.....	3,000 ^a	2,726	3,000 ^a	2,000 ^a	1,000 ^a	3,000 ^a	3,000 ^a	3,000 ^a	a	a	7,461	10,033	24,404	13,693	12,807	11,618	11,390	11,705	16,555
Georgia.....																			100
Maine.....	25,063	19,992	22,738	10,220	8,345	11,273	14,685	17,103	16,392	20,191	13,764	18,109	18,390	22,566	8,835	6,748	8,011	10,974	18,922
New Hampshire.....	30,343	30,964	16,517	12,573	8,718	12,425	12,119	15,490	26,494	28,831	25,555	34,414	38,589	52,219	46,544	44,000 ^a	42,632	48,319	63,579
New York.....	13,971	12,696	5,556	6,160	6,255	6,138	6,262	5,468	a	a	5,000 ^a	5,000 ^a	5,000 ^a	5,000 ^a	4,000 ^a	4,000 ^a	4,000	3,000	4,800
North Carolina.....	105,560	103,273	103,163	86,429	58,465	85,962	79,844	82,499	102,393	94,595	56,795	76,738	79,312	100,016	93,644	112,144	122,857	148,493	230,367
Pennsylvania.....					25	213	64	245	144	a	300 ^a	300 ^a	300 ^a	400 ^a	300 ^a	400 ^a	500	200	
South Dakota.....					6,067	3,220	9,190	22,099	34,144		42,297	48,328	54,692	59,015	56,499	70,913	64,806	68,374	74,540
Texas.....														100 ^a	100 ^a	100 ^a			200
Virginia.....					6,759	13,459	12,140	14,810	20,459	22,175	9,766	18,544	21,705	22,000 ^a	24,298	20,550	24,010	29,089	32,960
Wyoming.....	6,000 ^a	6,677	6,760	9,331					a	a	1,168	6,726	7,833	11,846	13,953	18,000 ^a	22,415	17,021	20,345
Maryland.....	2,349	2,624			90		500 ^a	100 ^a											
Massachusetts.....					a		100 ^a	100 ^a											
Minnesota.....																			
Nevada.....					50														
Undistributed.....	13,290	5,977	8,602	3,926	3,097	16,510	19,884	6,546	16,194	17,291	10,465	8,503	9,022	32,715	12,543	65,548			

^a Included in Undistributed. The figures shown are estimates by the author. All other figures from U. S. Bureau of Mines Minerals Yearbooks.

was not until 1709 that porcelain was made in Europe.* In that year Boettcher, at Meissen, Saxony, probably used feldspar in his product. The Ytterby feldspar mine in Sweden is said to have been opened in 1780 and was still in operation in 1925.⁸³

The most important world movements of feldspar have been as follows: Sweden to European countries, principally Germany, France, Great Britain, and Belgium; Norway to European countries, principally Germany, France, Great Britain, and Poland; Czechoslovakia to Germany, Austria, Rumania, and Poland; and Canada to the United States.

The duty on crude feldspar, originally \$1 per long ton under the Tariff Act of 1930, was reduced to 50¢ per long ton in 1932 after a cost-of-production investigation by the Tariff Commission, and later was further reduced pursuant to trade agreements. The duty on ground feldspar, 30 pct ad valorem under the Tariff Act of 1930, has also been reduced pursuant to trade agreements. Since Jan. 1, 1939, the rate on crude feldspar has been 25¢ per long ton and the rate on ground feldspar has been 15 pct ad valorem. These rates are presently effective under the General Agreement on Tariffs and Trade negotiated at Geneva, Switzerland.

PRODUCTION AND CONSUMPTION

DuBois³¹ reports that the first feldspar mining in United States was by Brainard and Clark in Connecticut in 1825. The crude spar was shipped in barrels to England. Bowles and Justice¹⁴ mention some feldspar shipped from North Carolina to England as early as 1744. Potteries in Trenton were using Cornwall stone from England in 1860; about that time they began getting Maine feldspar, according to DuBois.

The first feldspar mill in the United States was set up at the Toll Gate mine, south of Middletown, Connecticut, about 1850. It consisted of a set of chaser stones pulled around by oxen.

Statistical records are available from the year 1880. Between that year and 1898, production varied between 6,000 and 18,000 long tons. In 1899, the tonnage increased to 27,202, most of the increase being due to the new use of feldspar in scouring soaps. In 1903, production was 41,891 tons; in 1911, it was 92,700 tons; and in 1924, it had increased to 204,772 tons.⁸⁸ Production in 1946 was 508,380 tons (470,199 tons ground feldspar); and in 1947 it was 459,910 long tons of crude feldspar (482,700 tons ground feldspar). See Fig 4.

Production of crude feldspar usually is reported in long tons and consumption of ground feldspar is reported in about the same number of short tons. The difference of 240 lb represents approximately handling plus other losses in the grinding plant. There are also annual differences in accord with the difference in crude inventory at the vari-

* C. F. Binns in *The Americana*. New York, N. Y., *The Americana Co.*

ous mines and plants from year to year. Salient events in the feldspar industry in the United States have been:

1. First feldspar produced for shipment to England in 1825.
2. Beginning of the pottery industry about 1853.
3. First use of feldspar for artificial teeth, 1883.
4. Discovery in 1896 that alumina is a valuable constituent in glass. (This use developed very slowly, only 1 pct in 1913.)
5. Discovery of advantage of feldspar as base for scouring soaps, about 1897.
6. Use of considerable quantities of feldspar for poultry grit and roofing granules, which began about 1900. This use reached a peak of 20 pct of the total feldspar production in 1920, declining to less than 1 pct in 1935.
7. Feldspar first used as a binder in abrasive wheels in 1907.
8. During the first World War period, some high-potash feldspar was used in portland cement to increase the recovery of by-product potash. About the same time a few hundred tons of high-potash feldspar was shipped from North Carolina to a plant near Atlanta, Georgia, for extraction of potash by one of the patented processes.²⁹
9. Manufacture of pottery classed as a nonessential industry during the first World War.
10. Stimulation of pottery manufacture, especially floor and wall tile, by the building boom of 1923 to 1926.
11. Use of feldspar in container glass generally adopted by largest manufacturers in 1924.
12. Magnetic separation and granular glasspar production starting in 1929 made feldspar a more desirable raw material for manufacture of glass.
13. Nepheline syenite imports started in 1936 and rapidly expanded following completion of the grinding plant at Rochester, New York.
14. Production of aplite started in 1938 and soon became important competition for feldspar because it furnished lower-cost alumina for glass.
15. Pilot-plant operation of flotation process in 1940 indicated greatly reduced production cost for glass feldspar.
16. First commercial froth flotation plant started large-capacity production at Kona, North Carolina, in 1946.

Fig 2 shows production and consumption of feldspar in the United States according to states and Table 4 lists the data.

Production was first recorded in Canada in 1890, when 700 tons of crude feldspar was shipped to the United States. The maximum Canadian production was attained in 1924 with 44,804 tons. Production

dropped from 37,527 tons in 1929 to 6,921 tons in 1932, and increased to 36,369 tons in 1946. Of this, 85 pct was exported to the United States in 1924; 80 pct in 1929; 29 pct in 1932; 63 pct in 1935, and 53 pct in 1946. Canada has large reserves of feldspar, and production could be increased to meet any probable demand.²³

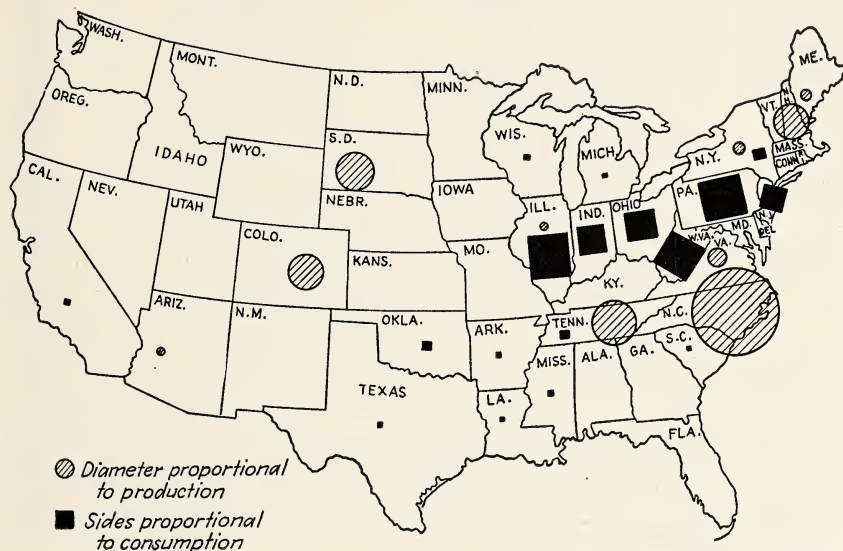


FIG 2—PRODUCTION AND CONSUMPTION OF GROUND FELDSPAR IN THE UNITED STATES IN 1946.

Table 5 shows world production of feldspar for the years 1931 to 1944 inclusive.

PROSPECTING, EXPLORATION AND MINING

Feldspar has been found outcropping at surface in so many parts of the world, in reasonable proximity to consuming areas, that little prospecting and exploration for commercial deposits have been required. In pegmatite-bearing areas, new deposits have repeatedly been found by simple methods involving for the most part only hand labor. A great deal of effort, however, if not so much money, has been wasted by the failure of prospectors and miners to use the most elementary principles of mining in opening up deposits. Watts called attention to this in 1916.⁹³

Rapid development of the feldspar in western North Carolina in the 1920s resulted from a combination of circumstances. Mica mining had been carried on for 50 years, so that most of the mica miners knew the rudiments of mining. Several feldspar companies put in wagon scales at the railroad sidings and started buying feldspar. In a short time there were wagonloads of feldspar coming out of most of the mountain roads.

TABLE 4—*Production and Consumption of Ground Feldspar, 1946*

Production		Consumption			
State	Tons	State	Tons	State	Tons
Arizona.....	8,400	California.....	8,641	Michigan.....	3,500
California.....	294	Illinois.....	68,737	Minnesota.....	1,496
Colorado.....	55,251	Indiana.....	47,756	Mississippi.....	4,600
Connecticut.....	15,000	Maryland.....	18,374	Missouri.....	1,000
Illinois.....	4,000	Massachusetts....	3,009	Arkansas.....	8,000
Maine.....	14,822	New Jersey.....	41,340	Colorado.....	500
New Hampshire...	53,000	New York.....	19,420	Connecticut.....	1,500
New Jersey.....	7,464	Ohio.....	47,031	Kentucky.....	1,500
New York.....	15,000	Oklahoma.....	14,411	Louisiana.....	3,000
North Carolina...	143,027	Pennsylvania.....	70,706	South Carolina...	3,000
Tennessee.....	64,500	Tennessee.....	18,337	Florida.....	1,000
South Dakota.....	59,441	West Virginia....	66,024	Texas.....	7,000
Virginia.....	30,000	Wisconsin.....	10,317		
Total.....	470,199			Total.....	470,199

At first the mining was done largely in the winter, when the crops were in, but many farmers found that they could make more out of feldspar, or liked mining it better than farming, so feldspar mining became a year-round occupation.

These farmers located the feldspar in old mica mines, by rock outcrops, or by digging where float was found. In many mines, weathering extends some distance down, so that much of the feldspar was recovered at first with hand tools. Eventually the miners got down to where drilling and blasting became necessary, also hoisting and pumping.

During the years 1932 to 1940, the larger mines were taken over as "company" operations, or by stronger "contractors." The day of the wagon mine was past and comparatively few independent contractors are still mining in western North Carolina.

The prospecting now done is performed usually by a crew hired for the purpose and equipped with a portable compressor and pneumatic drill. Often, a bulldozer is used to remove soil and loose rock. When shafts are sunk for test purposes, hoists and pumps are used. The largest companies have done some core drilling but this is not generally a part of the prospecting program.

Most of the feldspar mines are opencut or quarry operations during the entire life of the mine. A few with too much overburden are worked through tunnels or shafts.

After the deposit has been prospected, opened and equipped for mining, the most important part of the operation is cobbing. A few deposits have been found containing feldspar clean enough to be shipped

FELDSPAR

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TABLE 5—World Production of Feldspar,^a 1931–1944

Country	Metric Tons (3205 Lb)													
	1931	1932	1933	1934	1935	1936	1937	1938	1939	1940	1941	1942	1943	1944
United States.....	149,480	106,396	153,051	156,663	192,592	248,654	272,842	199,267	257,534	295,480	344,299	321,240	313,126	332,663
England ^d	60,000	60,000	60,000	60,000	60,000	b	b	b	b	b	b	b	b	b
Sweden.....	33,113	23,693	32,567	34,468	b	56,799	49,140	45,111	40,792	22,232	b	b	b	b
France.....	10,700	b	b	b	b	b	8,900	b	b	b	b	b	b	b
Czechoslovakia ^d	30,000	30,000	30,000	30,000	16,702	16,190	19,365	12,753	11,306	19,464	23,623	20,203	21,644	23,509 ^f
Canada.....	16,640	6,393	9,669	16,603	24,229	29,985	32,555	21,761	21,282	b	b	b	b	b
Norway.....	15,105	13,015	17,986	22,139	b	b	b	b	b	b	b	b	b	b
Russia.....	5,000	3,550	4,490	6,808	b	9,524	9,986	10,419	b	b	b	b	b	b
Germany.....	4,750	5,217	4,861	7,637	b	8,620	13,437	13,391	12,473	b	b	b	b	b
Italy.....	3,068	681	1,309	1,026	b	1,960	2,587	1,690	b	b	b	b	b	b
Rumania.....	67	1,529	2,706	3,329	b	2,550	3,232	5,046	5,596	b	b	b	b	b
Finland.....	172	369	376	431	b	1,082	1,346	620	1,051	1,220	2,981	5,632	b	b
Argentina.....	209	1,022	2,609	891	166	101	162	178	51	64	452	1,469	b	b
Australia.....				212	315	553	669	502	615	1,072	1,081	1,026	522	b
New South Wales.....				1,845	b	3,097	2,947	2,919	2,853	3,561	4,173	3,304	2,351	8,000 ^g
South Australia.....				6,000	b	b	b	b	b	b	b	b	b	b
Western Australia (exports).....				b	b	b	b	b	b	b	b	b	b	b
So. America (exclusive of Argentina) ^e				b	b	b	b	b	b	b	b	b	b	b
Japan.....				60	72	45	158	199	74	138	52	19	32	b
Egypt.....	26	179	60	b	b	b	798	495	501	b	1,257	2,100	b	b
India.....	339	481	688	638	b	1,403	b	702	b	b	b	b	b	b
China.....	b	26,858	27,189	27,780	b	b	b	b	b	b	b	b	b	b
Brazil.....	b	b	b	b	b	b	8,400	b	b	b	b	b	b	b

^a Production figures for 1931–1944, U. S. Bur. Mines Minerals Yearbooks. Data for China include Manchuria, from Mineral Trade Notes, U. S. Dept. of Interior (1936) 3, No. 1.

In addition to countries listed feldspar is produced in Madagascar, Palestine, and United Kingdom.

^b Data not available.

^c Principally Cornwall stone.

^d Estimated figures for Czechoslovakia and England 1931–1934, inclusive. Official figures of Czechoslovakia output are not available, but it is estimated that the annual production is approximately 30,000 metric tons (Stat. Comm. Czechoslovak Ceramic Soc.).

^e Production for 1934 from Chile.

^f From reference 23.

^g From reference 3.

as blasted from the mine but these are exceptions. In the great majority of places, the lumps made by blasting must be broken by hand with hammers, to remove quartz, mica, garnet, or other minerals. (Feldspar mines in the Spruce Pine district of North Carolina are described by Olson.⁷³)

Where it is not practicable to remove the quartz, grades are made containing different proportion of this mineral, but virtually all mica, garnet and other minerals must be removed from all grades of crude feldspar. In mines containing both soda and potash feldspar, these are generally separated. A separation is also made as to *soft* (semikaolinized) and *hard* spar.

Mica and quartz sometimes are important by-products, especially if the mica is in flat books of good size from which "sheet" or "pattern" mica is obtainable. Quartz seldom sells for enough to provide much margin over the separation and transportation cost.

Mining for Flotation

Mining of feldspar for subsequent treatment by the flotation process is much simpler and cheaper than for other use, because almost the entire pegmatite or alaskite is "ore." Wagon drills, power shovels and motor trucks are used. As much as 700 tons of pegmatite per day has been obtained from a single mine with one or two $\frac{1}{2}$ or $\frac{3}{4}$ -yd power shovels; and no hand labor is required from the blasting of several days supply to the loading of the "glass" or "fine ground" product into railroad cars.

Sometimes the surface material is removed prior to mining for flotation, by bulldozers or power shovels. Occasionally a "horse" of schist is found in the pegmatite and separately disposed of or avoided. For the most part, however, the entire deposit goes to the flotation plant and there, by chemical and physical means, the minerals are separated and feldspar, quartz and mica are obtained.

Royalty

Most companies have found it more economical to lease than to buy a feldspar property. Leases require the payment of a royalty per ton or of a percentage of the value at the mine. Leases vary in terms from one to 99 years but most are probably for 20 years for that is about as short a time as can be allowed in which to write off any large development cost or amortize a plant. Royalty generally is on a per ton basis of 50¢ for No. 1 grade and 25¢ for No. 2. On this basis, the royalty for No. 3 grade (pegmatite or alaskite) would be 10 to 15¢ per ton. Sometimes an escape clause is included, which provides for increase in royalty with increase of the annual average market price of feldspar.

Royalty for quartz usually is 10 to 15¢ per ton. Mica and other min-

erals usually are on a percentage of the selling price, ranging from 5 to 16½ pct; 10 pct being a good average.

For paying royalty and as a basis of purchasing crude feldspar, the following grades have been recognized:

Grades of Crude Feldspar Recognized for Royalty

No. 1 feldspar shall have not more than 68 pct silica content, not more than 0.10 pct iron as Fe_2O_3 , and a potash-soda ratio of at least 2:1.

No. 2 feldspar shall have not more than 72 pct silica content and not more than 0.10 pct iron as Fe_2O_3 .

No. 3 feldspar shall be any other analysis of feldspar suitable for milling but not within the specifications of No. 1 or No. 2 grades.

PREPARATION FOR MARKET

Usual European practice is to ship crude feldspar to mills situated in consuming centers. At these plants it is usually ground wet and trucked to neighboring consumers.

In the United States and Canada, only 3 of the 36 grinding plants are in consuming centers, 5 are at intermediate points, and the other 28 are in the actual mining areas.

In the United States, chaser-stone crushing and batch pebble milling was standard practice until 1916.⁹² Then the introduction of air separation and continuous pebble mills revolutionized milling methods.¹⁸

Following this, quality control by chemical analysis was experimented with and the first plant designed to produce blended feldspar products under laboratory control was built at Spruce Pine, North Carolina, in 1926.¹⁹

During the 1920s, glass manufacturers began to use greater tonnage of feldspar, and they objected to the dust in the pebble-mill product. Producers then installed rolls or cone crushers, which both added iron to the product; therefore magnetic separators were installed. These removed not only the abraded iron but also iron-bearing minerals such as magnetite, biotite, garnet, tourmaline, hornblende and muscovite. The resulting "granular glasspar" was a better product at lower cost.²⁰

The adoption of froth flotation may be of greater benefit to the industry and consumers of feldspar than any of the advances previously made. By this means even the waste material from previous hand-sorting operations may be utilized. The resulting product is lower in silica and iron-bearing minerals than could be produced by the most careful hand sorting.

The flotation process does not solve all the problems of feldspar production. Most of the large pegmatites or alaskites have a low potash-soda ratio (analyses 7 and 8, Table 2). This limits the market largely to the glass industry. However, producers of such material have been

promoting research in the use of feldspar with a low potash-soda ratio in other ceramic industries, particularly white ware, and some progress has been made. In Georgia, large deposits of graphic granite are being developed which have a high potash-soda ratio. Analysis 22, Table 2, is representative of these Georgia graphic granites. Analysis 23 is a flotation concentrate from Georgia rock.

According to Gould³⁹ it is common practice for European plants to use pegmatite for part of the quartz and all of the feldspar.

Fig 3 is a generalized flowsheet of a complete modern feldspar mill equipped to handle both mine-run pegmatite and hand-sorted feldspar, using froth flotation to clean the pegmatite and chemically controlled blending and fine grinding of products. Important by-products are glass sand, railroad sand, placing flint, potter's flint and ground mica.

Table 6 itemizes the total grinding equipment in the domestic in-

TABLE 6—*Types and Calculated Capacity of Pulverizing and Grinding Equipment Used in Feldspar Plants of the United States*

Number of Units	Type	Size of Units	Production Rate, Tons per Hour		Tons per Hour	Tons per Year ^a
			20-mesh	200-mesh		
2	Cone pulverizer	24"	3		6	36,000
9	Cone pulverizer	36"	6		54	324,000
3	Rolls	20' × 14'	4		12	72,000
6	Rod mills	5' × 10'	7½ ^b		45	270,000
20-mesh capacity.....						702,000
3	Conical mills	8' × 22"		0.80	2.40	14,400
9	Conical mills	8' × 30"		1.00	9.00	54,000
10	Conical mills	8' × 36"		1.35	13.50	81,000
12	Conical mills	8' × 48"		1.65	19.80	118,800
6	Conical mills	8' × 60"		1.90	11.40	68,400
2	Conical mills	8' × 84"		2.40	4.80	28,800
1	Conical mills	10' × 36"		1.50	1.50	9,000
4	Cylindrical mills	8' × 10'		1.50	6.00	36,000
4	Cylindrical mills	8' × 12'		2.00	8.00	48,000
1	Tube mills	4' × 16'		0.50	0.50	3,000
3	Tube mills	5' × 22'		0.65	1.95	11,700
2	Tube mills	5½' × 16'		0.80	1.60	9,600
3	Tube mills	6' × 24'		1.00	3.00	18,000
3	Tube mills	6½' × 18'		1.25	3.75	25,500
200-mesh capacity.....						535,800
Total capacity 200-mesh and 20-mesh.....						1,237,800

^a Year = 6000 hours.

^b Grinding capacity double this but rate shown is for flotation concentrates.

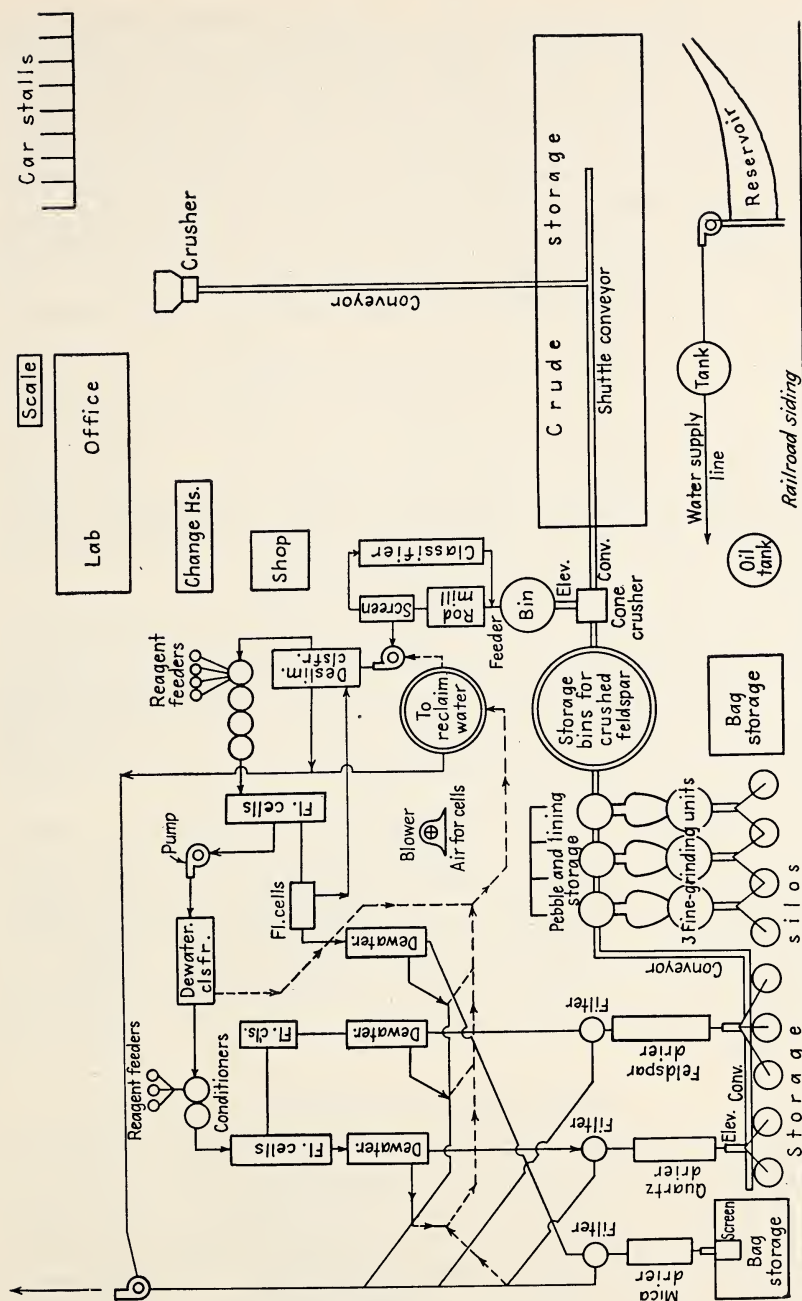


Fig 3—GENERALIZED FLOWSHEET OF FELDSPAR PLANT WITH FLOTATION AND FACILITIES FOR HANDLING SORTED FELDSPAR.

dustry that was operating and under construction during 1947. It also gives the average production rates in grinding the principal sizes, 20-mesh and 200-mesh. These are multiplied by 6000 to give annual capacity based on working 300 days of 20 hr each. These capacity figures may be considered excessive because they do not provide for peaks of consumption above the average that all industries must absorb. However, allowing 20 pct reduction for such peaks, the total still represents capacity approximately 100 pct above the maximum domestic consumption of ground feldspar in any year to date.

The wet-grinding practice in Europe until about 1920 was practically the same as had been used since the beginning of the industry. It consisted in feeding 1 to 1½-in. crushed feldspar into wet-grinding pans or pan mills 12 to 14 ft in diameter, with floors of hard china stone or granite blocks. Grinding in this type of mill is accomplished by stone chasers attached to radial arms. Enough water is added with the charge to make a thin sludge. After a batch is ground for the required period, it is washed out through a launder to "micas" (a series of troughs) and thence to settling pits and storage.

Since the first World War, pebble mills have been introduced in a few European plants. All are run wet, and most are batch mills. A few conical mills are in use in closed circuit with rake or bowl classifiers. An automatic hydraulic classifier has been used successfully with mills of both the pan and cylinder type. These are said to be producing to specifications such as all minus 180-mesh, 16 to 17 pct plus 600-mesh and 50 pct minus 1000-mesh.

In Czechoslovakia, run-of-mine pegmatite is separated by air selection and screening methods to provide a feldspar product for ceramic use. The separation of mica is effected by passing the oversize product from pebble-mill air separators through a series of burlap screens, which catch the mica and permit the feldspar to pass through. Quartz is removed by taking out of the air-separator circuit certain sizes that have been found to contain quartz segregations. A reduction of silica from 78 to 73 pct is made.

TESTS AND SPECIFICATIONS

Bowles and Justice¹⁴ record the first movement toward standard specifications for feldspar with the classification of grades at No. 1, No. 2 and No. 3 in 1906. However, as they say, "little progress in grading was made for many years. Most consumers designated the kind of spar they desired simply by its geographic source." The first chemical laboratory in the industry was installed at the plant of the Tennessee Mineral Products Co. at Bristol, Tennessee, in 1923. Beginning with this, serious efforts were made toward production of feldspar of uniform chemical composition and definitely limiting the content of impurities. This was the beginning of chemical control in the industry.⁵¹

A Feldspar Grinder's Institute was organized in 1929 and at its first meeting, on July 15 of that year, it was agreed that standardization of the product should be its first objective. This was accomplished through cooperation of the National Bureau of Standards, Division of Trade Standards. The standard classification compiled by a committee composed of representatives of both producers and consumers was circulated to a large majority of producers and consumers. Most of these endorsed the proposed standard and accordingly it became effective Sept. 1, 1930, as Commercial Standard CS23-30.⁶⁹ Feldspar was the first mineral or raw material to be so standardized.

Commercial Standard CS 23-30⁶⁹

The essential features of the Standard are:

I. SCOPE

This commercial standard classification covers ground feldspar used in the production of ceramic products, based on particle size and chemical composition. It is to be regarded as a classification rather than a definite purchase specification.

II. GENERAL REQUIREMENTS

All screen tests shall be made on standard screens (U. S. standard sieve series), the opening sizes of which are appended in Table 1. The standard method of screen testing is described on page 4, CS23-30. The standard method of chemical analysis is described beginning on page 4, CS23-30.

III. DETAIL REQUIREMENTS

A. Physical Classification Based on Fineness of Grinding¹

TABLE 1

United States standard sieve series No.	Percentage remaining on No. 200 sieve	Maximum per- centage on sieve designated	United States standard sieve series (opening in inches)
230	0.00- 0.35	1.0	.0024
200	0.35- 1.00	1.0	.0029
170	1.00- 2.50	1.0	.0035
140	2.50- 5.00	1.0	.0041
120	5.00- 9.00	1.0	.0049
100	9.00-14.00	1.0	.0059
80	14.00-21.00	1.0	.0070
60	21.00-30.00	1.0*	.0098
40	30.00-42.00	1.0*	.0165
20	42.00-62.00	1.0*	.0331
20 SG	62.00-85.00*	1.0*	.0331
20 G	85.00-100.00*	1.0*	.0331

¹ Fineness classification shall be made on a basis of the percentage remaining on the standard 200 sieve and that remaining on the sieve designated. Example: 140-mesh product will have 2.5 to 5.0 per cent remaining on the 200-sieve and less than 1 per cent on the 140-sieve.

* Changes and additions since 1930.

B. Chemical Classification Based on Composition as It Influences Use

The numbers designated herein are for the purpose of illustration and the various groups may be added to, up and down the scale, to provide for all commercial grades of feldspar.

Group 1

The first group includes the commonly accepted ceramic or body grades based on silica content and alkali ratio and containing less than 4 per cent soda (Na_2O) content.

The silica number and ratio numbers are to be used in combination. For example: Grade No. 67-51 designates a spar of silica content 66.00 up to 67.99 per cent and with 5 or more parts of potash (K_2O) to 1 part of soda (Na_2O).

Number	Silica (SiO_2) content in per cent
65	64.00-65.99
67	66.00-67.99
69	68.00-69.99
71	70.00-71.99
73	72.00-73.99
	Potash (K_2O)-soda (Na_2O) ratio
61	6 or more potash to 1 soda.
51	5 potash to 1 soda up to 6 potash to 1 soda.
41	More than 3 and less than 5 potash to 1 soda.
31	3 or less potash to 1 soda.

Group 2

The second group includes the spars used chiefly for glazing purposes which are based on soda content and contain 4 per cent or more soda (Na_2O).

Number	Soda (Na_2O) content in per cent
4	4.00-4.99
5	5.00-5.99
6	6.00-6.99
7	7.00-7.99
8	8.00-8.99

Group 3

The third group includes the spars used for glass-making purposes and are based on silica, alumina, and iron content.

The numbers are to be used in combination: For example, grade 69-17-X represents a grade of spar of 68.00 to 69.99 per cent silica, 17.00 to 17.99 per cent alumina, and with a maximum of 0.10 per cent Fe_2O_3 content.

Number	Silica (SiO_2) content in per cent
65	64.00-65.99
67	66.00-67.99
69	68.00-69.99
71	70.00-71.99

Number	Alumina (Al_2O_3) content in per cent
15	15.00–15.99
16	16.00–16.99
17	17.00–17.99
18	18.00–18.99
19	19.00–19.99
	Iron (Fe_2O_3) content in per cent
X	A maximum of 0.10
XX	0.10–0.20*
XXX	Above 0.20

* Revised since 1930.

IV. STANDARD METHODS OF TEST

A. Physical Test

Mesh or fineness.—A 100 g. portion of the dry sample is weighed out to an accuracy of 0.1 g. It is then transferred to a number 200 sieve and over a sieve pan which fits closely. The pan shall contain sufficient water to reach within not less than one-fourth inch or more than three-fourths inch from the top of the pan. The sieve and pan shall be vibrated or shaken in such a manner that water in the pan is splashed on the screen from below, so as to wash the powder about and cause the material that can pass through the sieve to pass into the pan below. This treatment shall be continued until no appreciable amount is passing through. The contents of the screen are then washed into a pan and thoroughly dried. The dried material is then placed on the coarsest sieve to be used. The finer screens, including the number 200, are placed in order of size under the coarsest, the number 200 being at the bottom. The tier of screens is then shaken until no more than 0.05 of a gram passes any screen after one minute of shaking each time. This point is determined by weighing the residue on the coarsest screen, reshaking for a minute until finished, then going to the next size and repeating the process.

B. Chemical Tests

General

Feldspar is analyzed for SiO_2 , " R_2O_3 ," Al_2O_3 , Fe_2O_3 , CaO , MgO , Na_2O , and ignition loss. SiO_2 , " R_2O_3 ," CaO , MgO , K_2O , and Na_2O are determined in 0.5 g. samples. Ignition loss is determined in a 5 g. sample. Fe_2O_3 is determined potentiometrically in a 10 g. sample, and the result is subtracted from the percentage of " R_2O_3 " to give Al_2O_3 . The result for the latter will of course include constituents such as TiO_2 , ZrO_2 , P_2O_5 and the like.

Accurate results in the analysis of feldspar are not easy to obtain, especially in the cases of SiO_2 and " R_2O_3 ." Attention must be paid to all details. Variations in check analyses should be within the following limits: SiO_2 , 0.2 per cent; " R_2O_3 ," 0.2 per cent; CaO , 0.05 per cent; MgO , 0.05 per cent; K_2O plus Na_2O , 0.2 per cent.

Analyses should be repeated if the summation does not fall between 99.75 and 100.5 per cent.

Analyses of potash feldspars should be checked against the Bureau of Standards standard sample No. 70 and analysis of soda feldspars should be checked against the Bureau of Standards standard sample No. 99. All results should be corrected by blank runs on reagents and factors should be calculated from the current International Table of Atomic Weights.

Procedure

Preparation of Sample.—The sample should be ground to pass a No. 100 screen and then well mixed. All samples for analysis must be taken from material that has been dried at 105° to 110° C.

Ignition Loss.—Weigh a 5 g. sample in a 30 ml. platinum crucible. Cover the crucible with a well-fitting cover, and heat for 15 minutes at 1,000° C. The heating can be done over a burner or in a muffle, and should be sufficiently gentle at the start so that there is no danger of mechanical loss. Cool over a good desiccant and weigh. The loss in weight multiplied by 20 represents the per cent of ignition loss.

The method of chemical analysis is too long to be given here. At the time of its adoption (1930) a complete chemical analysis of feldspar took 3 to 4 days. Simpler methods have since been developed,⁵⁵ so that now the same information is obtainable in 4 to 6 hr.

CS23-30 did not give a method of fusion test because no method for making such tests has been found generally acceptable. This does not mean that a fusion test is not important. Feldspar forms the "glassy bond" that gives strength to the fired ware, and in the glaze it provides smoothness, hardness and transparency. Several test methods have been advanced and one was patented. Two styles are generally followed; either a small cup or mold of feldspar powder is formed with an organic binder and fired to a short cone or button, or the feldspar powder is formed in a mold like the standard pyrometric cones. The latter bend over as the temperature and time of firing increase. In both cases, pyrometric cones are usually fired close to the test specimens or on the same block. Fusion tests are to show color and fusibility but are dependable only for comparison with other samples tested under identical conditions.³² It is now generally agreed that a complete chemical analysis furnishes a better guide as to the fluxing action of a feldspar than any fusion test so far devised.⁸¹

A considerable amount of microscopic work^{61,86,90} has been done on feldspar with a view to determining the constituents more rapidly than can be done chemically, but no methods are in general use. Microscopic work has also been done to determine the percentage of fine particle sizes,⁸⁷ below the sizes readily obtained with the finest commercial testing sieve (325-mesh). Other methods of determining size percentages are by means of the Andrews elutriator,⁴ the sedimentation method,²⁷ and an air-analyzer method devised by Roller.⁷⁶

USES

Good china was not produced until the important fluxing feature of feldspar was discovered. Feldspar is today a basic raw material for the manufacture of virtually all burned clay products.

The use of feldspar in glass has continued to increase until now almost two thirds of all the feldspar produced is going to the glass indus-

try. The quantity of feldspar going into glass has increased from 93,000 tons in 1935 to 244,000 tons in 1945. This increase has taken place despite consumption by the glass industry of large tonnages of competitive nepheline syenite (50,000 tons in 1945) and aplite.

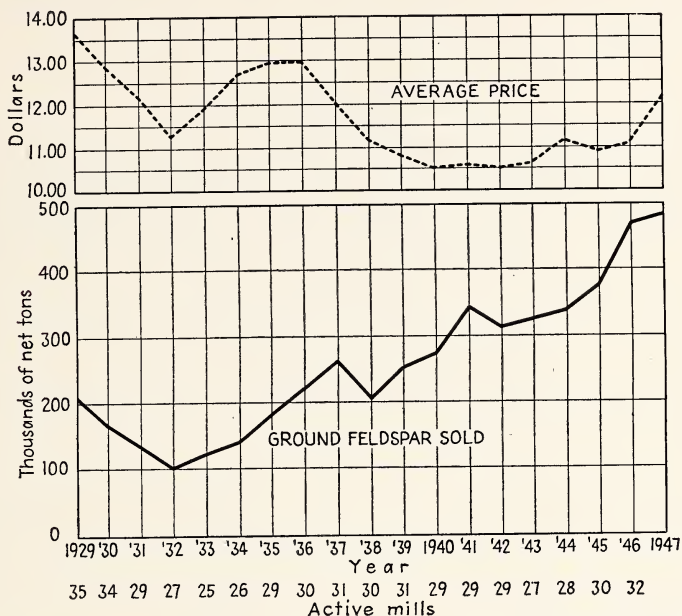


FIG 4—GROUND FELDSPAR SOLD BY MERCHANT MILLS IN THE UNITED STATES, WITH AVERAGE PRICES, 1929–1947.

From Minerals Yearbook, U. S. Bureau of Mines.

During World War II, the enamel industry was curtailed and largely diverted to the manufacture of other products. The postwar outlook for the enamel industry is very good and it is expected that the consumption of feldspar in enamel will soon resume its prewar position.

Table 7 gives typical formulas of manufactured products in which feldspar is an important ingredient.

Other uses of feldspar are in soaps and scouring powders, as a binder in abrasive wheels and in dental porcelain. Of these, the prospects for increased sales are best for scouring soaps and powders.

MARKETS AND PRICES

Excepting two or three years during World War II, when labor shortage curtailed production of crude and also limited mill production, there has long been a great excess of producing capacity in the feldspar industry. In 1945, when 30 mills were operating with an output of 373,000 tons, production was less than 50 pct of capacity.

Since that time two large plants have been completed and two are

under construction. These will increase the total grinding capacity of the industry to 1,200,000 tons, or approximately $2\frac{1}{2}$ times the estimated sales of ground feldspar in 1947.

Fig 4 shows tonnage of ground feldspar sold by merchant mills in the United States from 1929 through 1947 and Tables 8 and 9 give further details.

TABLE 7—*Ceramic Batch Formulas*^a

PERCENTAGES

Material	Semi-vitreous China	Hotel China	Floor Tile	Wall Tile	Sheet-iron Enamel	Electrical Porcelain	White-ware Glaze	Container Glass	Flat Glass
Feldspar.....	16	17.0	55.0	11.0	30.0	35.0	44.4	15.2	10.34
Flint.....	30	37.0	10.0	33.0	20.0	25.0			
Ball clay.....	29	20.0	15.0	27.0		20.0			
China clay.....	25	25.0	20.0	29.0		20.0	4.3		
Magnesium carbonate.....		0.5							
Whiting.....		0.5					20.4		
Borax.....					26.0				
Soda ash.....					4.0			16.2	20.74
Soda niter.....					3.0				
Fluorspar.....					3.0				
Cryolite.....					11.0				
Antimony oxide.....					3.0				
White lead.....							24.8		
Zinc oxide.....							6.1		
Sand.....								47.6	51.80
Limestone.....								18.1	15.55
Salt cake.....								0.47	1.57
Copper sulphate.....								2.43	

^a For additional formulas, see *Ceramic Industry* for January 1947.

TABLE 8—*Ground Feldspar Sold by Merchant Mills in the United States, 1929-1947*^a

Average			Average		
Year	Net Tons	Price	Year	Net Tons	Price
1929	209,808	\$13.73	1939	249,889	\$10.75
1930	167,380	12.95	1940	277,612	10.49
1931	132,542	12.30	1941	347,092	10.51
1932	104,289	11.27	1942	318,209	10.49
1933	126,418	11.80	1943	329,354	10.52
1934	136,820	12.66	1944	335,491	11.07
1935	189,289	13.00	1945	372,377	10.91
1936	222,126	12.99	1946	470,199	11.06
1937	263,387	12.10	1947	482,700	12.14
1938	206,646	11.20			

^a From Minerals Yearbook, U. S. Bureau of Mines.

TABLE 9—*Distribution of Sales of Ground Feldspar, by Industries, 1913-1945*

Use	Sales, Pct				
	1913	1930	1935	1940	1945
Glass.....	1	30	49	54	65
Enamel.....	9	9	9	9	4
Pottery.....	76	50	37	33	29
All other ^a	14	11	5	4	2

^a Includes scouring compounds, roofing and cement-facing granules, poultry grit, cement manufacture (for by-product potash recovery) and abrasives. Dental porcelain (false teeth) and the use as a ceramic binder for abrasive products is included under "pottery."

TABLE 10—*Current Prices of Feldspar^a*

Glass Feldspar				
Grade	20-mesh	Semigranular	Granular	40-mesh
16	\$11.00	\$11.00	\$11.75	\$11.50
17	11.75	11.75	12.50	12.25
18	12.50	12.50	13.25	13.00
19	13.25	13.25	14.00	13.75

Enamel Feldspar

Grade	100-mesh and Coarser	Finer than 100-mesh
70 pct and higher silica.....	\$14.00	\$15.00
Less than 70 pct silica.....	15.00	16.00

Pottery Feldspar, All Grades			Glaze Feldspar, All Grades		
200-mesh and Coarser	230-mesh	325-mesh	200-mesh and Coarser	230-mesh	325-mesh
\$17.00	\$18.00	\$19.00	\$19.00	\$20.00	\$21.00

^a From price list of United Feldspar and Minerals Corporation, New York, N. Y.

These prices are per ton of 2000 lb in bulk carloads f.o.b. Spruce Pine, N. C.; in paper bags, \$1.50 per ton extra [recently increased to \$2 per ton]. Less carload, minimum 2 tons \$3 per ton advance; less than 2 tons, \$30 per ton plus paper-burlap bags at 12¢ each. All above grades and grindings (meshes) according to CS23-30.

Because of improvements in mining and processing, and excessive plant capacity, feldspar is unique among minerals in that it continues to sell at prewar prices. In fact, the prices in Table 10 are the same as those in the 1937 edition of this book.⁴⁴

Freight Rates—With several freight-rate increases, and no increase in the price of feldspar, freight rates are becoming an important item in the delivered cost of feldspar. The new feldspar plants in Georgia and Colorado were promoted largely on their advantage from a freight-rate standpoint in reaching markets in the South and Southwest.

FELDSPAR SUBSTITUTES

Nepheline Syenite

Nepheline syenite is a quartz-free crystalline rock consisting principally of nephelite (a silicate of alumina, potash and soda) and albite and microcline feldspar. Canada and Russia are the only producing countries. In Canada there is only the large operation, the American Nepheline Corporation, near Lakefield, Ontario. In Russia large tonnages of nepheline syenite are mined for the recovery of apatite, with by-product production of nephelite.

For the United States market, Canadian nepheline syenite is shipped in crude lump form ($\frac{3}{4}$ -in.) to a grinding plant at Rochester, New York, where it is pulverized and its iron-bearing minerals, magnetite and biotite, removed by magnetic separation.

Most of the nepheline syenite has been used in glass as a substitute for feldspar but research has been active for several years on applications in other branches of ceramics. Commercial methods have been worked out to use nepheline syenite as an ore for production of aluminum.

Prices of nepheline syenite at Rochester are quoted as \$13.75 for glass grade and \$17.25 for ceramic grade.²⁵

Crude nepheline syenite enters the United States free of duty, provided total imports of crude and ground material do not exceed 50,000 long tons in any calendar year. The duty on ground nepheline syenite is 15 pct ad valorem.⁶⁷

Aplite

Aplite is produced at two grinding plants in Virginia, near Piney River, where there is a belt some 13 miles long containing this rock. It is composed principally of albite, zoisite and sericite and contains smaller amounts of microcline, quartz, titanite, apatite and clinozoisite. Most of the beneficiation is accomplished by discarding the fines. Calcining has been used as a means of lowering the pulverizing cost. The product is a low-cost source of alumina for glass where up to 0.5 pct combined iron and titania are not objectionable. Table 11 gives analysis of nepheline syenite, aplite and other feldspar substitutes.

TABLE 11—*Analyses of Feldspar Substitutes*²⁴
PERCENTAGES

Constituent	Aplite	Nepheline Syenite	Garspar	Kyanite	Slag
SiO ₂	60.64	60.22	94.1	37.70	38.52
Al ₂ O ₃	24.09	23.72	0.1	61.40	7.52
Fe ₂ O ₃	0.24	0.06	0.1	0.15	0.20
CaO.....	5.67	0.42	2.4	0.07	45.85
MgO.....		0.09	0.4	0.03	0.02
K ₂ O.....	2.52	5.04			0.97
Na ₂ O.....	6.30	10.06	2.6	0.18	
Loss.....	0.53	0.47	0.3	0.10	
As ₂ O ₅			0.1		
F.....					2.62
P ₂ O ₅					1.03
Ma ₂ O.....					0.44
Mn.....					0.12
SO ₃					0.59
C.....					0.10
Total.....	99.99	100.08	100.1	99.78	97.98

OUTLOOK FOR THE FUTURE

There is a possibility that within a few years practically all commercial production of feldspar in the United States will be by the froth flotation process. When a quartz-free feldspar becomes generally available in large tonnage, almost all manufacturers of scouring compounds may substitute feldspar for the several other minerals now used. Other prospective future developments are the beneficiation of Arkansas nepheline syenite³⁴ and perhaps also of Wyoming leucite.⁷⁸ Use of titanium and flint in porcelain enamel may reduce the requirements of feldspar.

The United States Congress in 1947 recognized feldspar as a wasting national resource by allowing producers to take depletion charges up to 15 pct of their gross cost of production.

PATENTS

The following United States Patents relating to feldspar have been granted in the last twenty years.

- No. 1744967. Patented January 28, 1930. F. R. Johnson: Art of Separating and Apparatus Therefor.
- No. 1855115. Patented April 19, 1932. Charles H. Peddrick, Jr., and Philip Wager Lewis; Assignors to United Feldspar Corporation: Process for the Preparation of Feldspathic Flux for Porcelain (The "Chemical Control" Patent).
- No. 2007742. Patented July 9, 1935. Leslie Brown: Process of Making Ceramic Roofing Granules.

- No. 2062072. Patented November 24, 1936. Norman G. Smith and Stanton G. Smith: Purifying Feldspar.
- No. 2210254. Patented August 6, 1940. C. H. Peddrick, Jr. (Assigned to Feldspathic Research Corporation): Mineral Composition for Use in Glass Manufacture.
- No. 2260000. Patented October 21, 1941. B. C. Burgess and J. E. Boyd, Jr. (Assigned to Feldspathic Research Corporation): Ceramic Composition.

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CHAPTER 16

SECONDARY FERTILIZER MINERALS

By J. W. TURRENTINE*

SECONDARY fertilizer minerals include borax, gypsum and sulphur and such compounds as the sulphates of copper, magnesium, manganese and zinc; also the carbonate and oxide of magnesium. Potash, phosphates and nitrogen are generally considered to be primary fertilizer materials.

The growing plant, under the average conditions of growth, is able to get from the soil the mineral elements required for the completion of its life cycle. The elements taken up are numerous and the vital functions of some of them yet remain to be determined. However, in the commercial growing of the plant (farming) something much more than the mere completion of a life cycle is required. There the maximum possible growth of plant or yield of seed or fruit are the objective and for that objective the average soil is deficient in some elements, and additions from artificial sources are desirable. Commercial fertilizers (15,000,000 tons in 1946) are designed to supply those deficiencies.

Long experience has taught that nitrogen, phosphorus, and potassium are the elements most apt to be required and in a greater degree, and to supply them is the basic function of the fertilizer industry. Thus nitrogen, phosphate, and potash are designated as the major plant-food materials.

But other mineral crop nutrients may likewise be deficient in varying degrees as determined by diagnostic techniques, soil tests, plant analysis and foliar symptoms,³ calling for their addition from artificial sources if maximum crop yields are to be obtained. Because used in lesser amounts and frequently in relatively minute amounts as compared with the major three, they are designated either as "minor elements," or, if used in larger amounts, as "secondary elements."

Thus, included under the two designations, in alphabetical order, are: borax; copper sulphate; magnesium carbonate, oxide and sulphate; manganese sulphate, and zinc sulphate. Obviously, the sulphates of the metals copper, manganese, and zinc cannot be considered as "industrial rocks," but they are given brief mention for whatever interest may pertain thereto.

* President Emeritus, American Potash Institute, Washington, D. C.

Then, there is the further category of minerals used in agriculture not so much as plant nutrients as for their beneficial effects on the soil itself, which includes limestone, both calcic and dolomitic and derivatives, gypsum and sulphur.

LIMESTONE

Limestone takes precedence in tonnages over all other industrial minerals and rocks used in agriculture according to the release on Approximate Consumption of Liming Materials on United States Farms during 1946, issued jointly by the National Lime Association and the Agricultural Limestone Division of the National Crushed Stone Association, a total of some 29,462,000 tons of liming materials having been consumed in that year, classified as follows: limestone, 27,832,547 tons; burnt lime, 156,805; hydrated lime, 265,780; marl, 552,098; miscellaneous,* 654,970.

Ordinarily, limestone is not classified as a fertilizer, its use being designed principally to adjust soil acidity (pH) to the optimum level for a specified crop rather than to supply crop food. For such purposes, it is ground to various degrees of fineness and spread broadcast, commonly at the rate of a ton per acre, as prescribed by soil tests or farmer experience. Distribution varies widely among the several agricultural areas, 19,500,000 tons being used in the eight north central states as against only 1,700,000 tons in the nine southern states, reflecting the requirements of the legumes, which are grown much more commonly and extensively in the former than in the latter group of states.

However, since limestone contains varying amounts of magnesia, and there is no sharp differentiation in trade terminology between the high (dolomitic) and low magnesian limestones, and further, since both calcium and magnesium are essential elements of plant food, and magnesium deficiency is widely recognized, it cannot be said that limestone is not fertilizer in the stricter sense of supplying crop nutrients, even though it is not ordinarily so considered. Further details are given under the heading Magnesium later in the chapter.

GYPSUM

The agricultural use of gypsum ("land-plaster") antedates that of other mineral fertilizers in general, its application to grass being one of Benjamin Franklin's numerous scientific ventures. By this token, its use antedates also the development of the agronomic and soil sciences. Subsequent research has failed to establish it as a crop nutrient, with perhaps the single exception of the peanut crop, where its use is well established and, according to recent research, where its function appears to be to provide nutrient calcium.

* Consists of ground mollusk and eggshells, paper and sugar-mill refuse, slag, lead-mine chats and carbide refuse.

Its major function is that of soil conditioner or supplement, and for this use, particularly in the reclamation of saline and alkaline soils, its chemical and physical reactions are a matter of scientific understanding, as set forth by W. T. McGeorge.⁶ There the problem is the replacement of sodium by calcium in the soil-colloid complex to obtain a granular, as contrasted with a gelatinous, soil structure amenable to cultivation. Such problems do not occur in the humid areas, at least to the point where gypsum is recommended for their correction. This purposeful use must account for most of the 450,000 tons of gypsum, valued at \$1,700,000, used in agriculture as such in 1945.

Nevertheless, in the humid areas gypsum is widely used as a constituent of phosphate; the common superphosphates of commerce average 50 pct gypsum. Thus, with the 1945 consumption of 6,600,000 tons of superphosphate, 3,300,000 tons of gypsum was used in American agriculture. This tonnage would appear to be ample for any incidental and unidentified benefits to accrue from its use in the humid areas. In the arid areas, the situation is quite different, both the functions and the benefits being well defined.

SULPHUR

While the element sulphur is recognized as a plant nutrient, situations rarely arise where it has to be supplied independently, as the sulphates are widely used in commercial fertilizers. As previously noted, gypsum constitutes 50 pct of superphosphate, in addition to which large tonnages of both ammonium and potassium sulphates are used in fertilizer mixtures. Also, elementary sulphur is used extensively in the manufacture of fungicides and insecticides as dusts and sprays and finds its way ultimately into the soil. In the year 1945, manufacture of fertilizers required 2,800,000 short tons of sulphuric acid (basis 100 pct), which, combined with elementary sulphur used in insecticides, accounted for the consumption of 600,000 long tons of sulphur used for agricultural purposes.⁴ In addition, there are, in the aggregate, vast additions from sulphur fumes in the atmosphere brought down into the soil by rain, particularly in industrial areas. These sources, in general, supply adequate quantities of nutrient sulphur.

The major function of elementary sulphur when added to the soil is that of a soil corrective for the neutralization of excessive alkalinity. As stated by McGeorge:⁶

"Sulphur offers the greatest competition to gypsum in the group of alkali soil correctives. It oxidizes readily in the soil to sulphuric acid. This provides for neutralization of excess alkalinity and, due to the reaction between this sulphuric acid and calcium carbonate, it supplies soluble calcium in the form of calcium bicarbonate and calcium sulphate for the replacement of absorbed sodium. One part sulphur is

equivalent to five parts gypsum in reclamation. It acts more slowly than gypsum because it must be oxidized by soil microflora before it is of any value."

BORAX

The agricultural use of borax (and in lesser amounts, boric acid) as a boron carrier has had a phenomenal growth in recent years, an increase from 1600 tons in 1941 to more than 7500 tons in 1946. In contrast to a situation of only a few years ago, when it was regarded with suspicion as being toxic, it is now recommended for use by the agricultural officials of 33 states.² Recommendations prescribe its use at rates varying from 5 to 60 lb per acre, depending on the crop and the degree of deficiency of the soil on which it is grown. While effective on a long list of crops, it is particularly so on alfalfa; before the discovery of boron as an essential and limiting factor, alfalfa could not be grown successfully in large areas. Since the establishment of the fact that boron deficiency is so widespread, many commercial fertilizer mixtures contain a small percentage of borax as added insurance that the other plant foods contained therein can yield their anticipated profitable returns.

Formerly refined borax and boric acid supplied that agricultural requirement for boron but recently a new "fertilizer borate" has appeared on the market, which is a partially purified material produced through a special concentrating process particularly designed to meet the sizing requirements of the fertilizer trade. Although less pure than the refined borax, it is still only slightly less concentrated in the element boron and is becoming established as an acceptable supplement to current supplies.

COPPER SULPHATE

The agricultural use of copper finds its widest application to soils high in organic matter, as typified by the Everglade soils of Florida. There its use can give phenomenal results; for example, when applied to sugar cane at the rate of 75 to 100 lb per acre in the form of copper sulphate. Its value is recognized also in the fertilization of citrus crops grown on mineral soils in both Florida and California. The latest (1937) figures available on the use of copper sulphate as a crop nutrient indicate a consumption of 2500 tons.⁷

However, the widespread use of copper sprays, such as Bordeaux mixture, adds copper to soils where in some instances it may function as a plant nutrient and mask copper deficiency even if it exists.

MAGNESIUM CARBONATE, OXIDE AND SULPHATE

The nutritive role of magnesium in crop production is well established, as is likewise the fact that the native magnesium content of many soils has been depleted to the critical level of reducing crop yields.

Magnesium deficiency, indicated by foliar symptoms, is widely recognized.

Various magnesium compounds from various sources are used to supply that element, such as the magnesium carbonate of dolomite and other magnesian limestones; magnesium oxide from selectively calcined dolomite and brucite fines, and magnesite; sea water and the natural brines of Michigan. These products are basic materials of relatively low rates of solubility and consequently act slowly. However, in many situations, importance is attached to free solubility and neutrality, consequently there is an important market for magnesium sulphate in its various forms, hydrated (Epsom salts) and dehydrated, and as sulphate of potash-magnesia.

The foregoing materials constitute the major magnesium carriers of commerce. As shown by the survey conducted by Mehring and published in 1939,⁷ they, with other fertilizer materials containing various but usually minor amounts of magnesium, contributed a total of 1,600,000 tons of magnesium oxide in 1937.

Dolomite takes precedence in point of tonnage among the commercial sources of agricultural magnesium. The quantities of that element thus derived are difficult to estimate because of the frequent lack of differentiation between dolomite and limestone, the wide variation in magnesium content of limestones, and the many nonreporting, small-scale producers. From this it is evident that the addition of nutrient magnesium is only incidental, the major objective being the correction of soil acidity. A more specific use of dolomite is its inclusion in mixed fertilizers, the objective there being threefold; namely, to neutralize acids released in the soil by the fertilizer ingredients, notably ammonium sulphate, to supply nutrient magnesium, and to serve as a conditioner and filler. In 1945, some 500,000 tons of dolomite and limestone was so used.⁸

Magnesium oxide from the various sources mentioned possibly amounts to a current total annual consumption of some 8,000 to 10,000 tons averaging 80 to 90 pct MgO. It is sold under various trade names; as, for example, Actomag, derived from dolomite, and Michox, derived from the natural brines of Michigan.

Magnesium Sulphate—Prior to World War II, the principal sources of magnesium for plant food were the double sulphate of potash and magnesium and the dehydrated sulphate, kieserite, both imported from Germany as products of the German potash industry. Both importations had approximated 13,000 tons each when they were terminated upon the outbreak of European hostilities. Soon thereafter, however, a domestic source of the double salt was established by International Minerals and Chemical Corporation, one of the three potash producers operating in the Carlsbad area of New Mexico. This product, sold under

the trade name of Sul-Po-Mag, is derived from the natural potash mineral, Langbeinite ($K_2SO_4 \cdot 2MgSO_4$) by grinding and selective washing or leaching of the latter to remove its natural contaminant, sodium chloride.¹ Sul-Po-Mag contains 22 pct K_2O as potassium sulphate and 18 pct MgO as magnesium sulphate. Although its market price is determined more by its potash than its magnesium content, it is a valuable source of both elements, particularly where the former is desired in the sulphate form and the latter is required in the water-soluble and neutral form. Its current (1947) list price is \$14.50 per ton f.o.b. Carlsbad, New Mexico, a reduction from \$26 c.i.f. in 1946. This product has found ready acceptance, as indicated by sales in 1946 of some 120,000 tons per annum, reflecting a demand for both of its constituents. With the initiation of imports of German origin after the war, magnesium sulphate for agricultural use again appears on the list of imports, and under its familiar trade name of Emjeo is recovering its prewar position as an important source of magnesium sulphate.

MANGANESE SULPHATE

Manganese deficiency, like that of copper and of zinc, was first brought to widespread public notice as the result of spectacular demonstrations conducted in Florida, where mineral nutrient deficiencies frequently are acute in the muck, sandy and calcareous soils. Florida, therefore, stands far in the lead in the use of manganese as fertilizer for citrus trees, 1 pct (basis MnO) having been established as an essential ingredient of plant-food ratios officially recommended for that crop.

Manganese sulphate is the compound commonly used in agriculture. A major source is the Tennessee Eastman Corporation, a subsidiary of the Eastman Kodak Co., the first commercial producer.⁵ It is obtained as a by-product of other manufacturers and is marketed under the trade name of "Techmangan 65 pct." At the recommended per acre application of 50 to 100 lb of manganese sulphate, or of 3 to 5 lb per 100 gal of spray, consumption has increased to 14,500 tons per annum (1945). Of this total, 11,500 tons was consumed in Florida and 3000 tons in other states. In addition to this use as a crop nutrient, 5000 tons was used in animal feeds, making a total of 19,500 tons of manganese sulphate used in agriculture in that year.

ZINC SULPHATE

The crop requirement for zinc, like that for copper, is low, therefore zinc-deficient soils are seldom encountered. The exception again is the soil of Florida, which is notoriously deficient in the nutrient elements essential to plant growth. Likewise, the citrus groves of California have been shown to respond favorably to small applications of zinc in some

form. Spraying citrus trees with dilute solutions of zinc sulphate suffices to overcome the deficiency. In 1945, a gross weight of 6645 tons was used in agriculture. This tonnage, equivalent to 3880 tons dry basis, represented a 34 pct increase over that of the year 1944.⁹

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CHAPTER 17

FLUORSPAR AND CRYOLITE*

BY HENRY T. MUDD†

FLUORSPAR is a nonmetallic mineral aggregate or mass containing a sufficient quantity of fluorite (CaF_2) to be of commercial interest. It has only moderate value per unit of weight and its cost as a percentage of the cost of finished consumer products is nearly negligible. Nevertheless, it has wide and great industrial importance. In periods of national emergency it is a mineral without which many very necessary manufacturing processes would be greatly handicapped; a few could not exist.

Fluorite contains 51.1 pct calcium and 48.9 pct fluorine. Industrial grades of fluorspar prepared for the consumer normally contain from 85 to 98 pct fluorite, depending on the use. The ores may contain as little as 30 pct fluorite, depending on many factors such as accessibility to transportation and markets, character of ore, and prices.

Fluorite is a lustrous, glasslike mineral, generally translucent to transparent; it may be clear and colorless or range in color from slightly bluish through various shades of violet, amethyst, purple, green, and yellow. It crystallizes in the isometric system and possesses perfect octahedral cleavage. Commonly it occurs in masses of very pure crystalline material with aggregates of cubical crystals in open spaces, but it is also found in fine to coarse granular form. Banded veins and masses with fibrous, radiating structure occur locally. It is usually found associated more or less intimately with other minerals and rocks, from which it must be separated for commercial use.

The specific gravity of fluorite is 3.18 and the hardness is 4 in the Mohs scale, compared with 7 for quartz and 3 for calcite. It is distinguished from calcite by its failure to effervesce with dilute hydrochloric acid. Heated with sulphuric acid, it gives off fumes of hydrofluoric acid, which etch glass.^{22,25,33,34,35,41}

* This chapter is a revision of the one on Fluorspar and Cryolite by Ernest F. Burchard in the first edition of this book (1937). The author is greatly indebted to Hubert W. Davis, of the United States Bureau of Mines; to James S. Williams and Ralph E. Van Alstine, of the United States Geological Survey, and to A. E. Gaydos, of the Pennsylvania Salt Manufacturing Co. The Minerals Yearbooks published by the Department of the Interior were heavily drawn upon.

† Consulting Mining Engineer, Los Angeles, California.

GEOLOGY AND DISTRIBUTION OF FLUORSPAR DEPOSITS

Fluorite is a rock-forming mineral that occurs in various associations. It is most abundant in veins, especially in sedimentary formations, but also is found as a minor accessory in granite, syenite, pegmatite, gneiss, schist, and volcanic rocks. Lindgren²⁹ regards it as a "persistent mineral" or one of a group of minerals, few in number, that are less sensitive than others to physical conditions and that form under a great variety of conditions. Such minerals are generally of simple composition; they do not contain the hydroxyl molecule, and include quartz, hematite, pyrite, chalcopyrite, fluorite, calcite and native gold. Fluorite is a common primary gangue mineral of ore deposits (and a common accessory mineral of their wall rocks) including those formed at various depths and temperatures by magmatic segregation, contact metamorphism, and deposition in veins from circulating hydrothermal solutions. Fluorite is commonly found in sedimentary rocks, frequently with galena and sphalerite, in deposits formed at moderate or shallow depths, either by solutions from a deep-seated source, as believed by some, or by meteoric water, as contended by others. Fluorspar in sedimentary rocks includes the large deposits of the Illinois-Kentucky district in the United States, those of Durham and Derbyshire in England, and those of the Madoc district in Ontario, Canada.

Minerals commonly associated with fluorite are calcite, barite, quartz, galena, and sphalerite. As with most mineral deposits, the most important geological features to be considered in connection with the localization of fluorspar deposits are structure and availability of suitable host rocks. Most fluorspar veins occupy fault fissures; some deposits in sedimentary beds are replacements influenced by local structure and by the composition and texture of the enclosing rocks. The source of deposits in veins in igneous rocks and in sedimentaries is generally believed to be magmatic. By some, the source is thought to be the enclosing rock.

Fluorspar occurs on every continent and in all of the following countries there has been substantial commercial production: Argentina, Australia, Canada, China, Chosen, England, France, Germany, Italy, Mexico, Newfoundland, Russia, Spain, Tunisia, Union of South Africa, the United States.

Fluorspar Deposits in United States

Fluorspar is found in many eastern and western states but in comparatively few of them are the deposits of commercial value. The largest thus far discovered are those of southern Illinois and northwestern Kentucky, comprising the well-known Illinois-Kentucky fluorspar field. Deposits of lesser importance have been worked in central Ken-

tucky, central and eastern Tennessee, and New Hampshire. A number of other localities are known in the eastern states but from none of them has there been a sustained production. Colorado and New Mexico are the principal western sources. During the recent war, no new important districts were discovered.

ILLINOIS-KENTUCKY DISTRICT

The Illinois-Kentucky district^{2,3,12-15,43} is the largest fluorspar-producing area in the world. The district, about 700 square miles, comprises most of Hardin and Pope Counties in Illinois and of Crittenden, Livingston and Caldwell Counties across the Ohio River in Kentucky.

The area is underlain by nearly horizontal Mississippian limestones, sandstones, and shales. It is characterized by a large number of steeply dipping normal faults and by the presence of dikes of much altered mica periodotite and lamprophyre. There are two types of fluorspar deposits: (1) nearly vertical veins occupying fault fissures, and (2) nearly horizontal, tabular or lenticular bodies.

The vein deposits, typically developed near Rosiclare, Illinois, and Marion, Kentucky, cut sharply through the formations and generally exhibit a more distinct and firmer footwall than hanging wall. The amount of displacement along the faults varies from a few feet to over 1000 ft but the largest deposits do not occur in the faults of greatest displacement. The Rosiclare fault has been traced for about $4\frac{1}{2}$ miles along the strike, and the vein formed in it has been mined underground for a distance along the strike of about 9000 ft. The veins vary in width from a fraction of an inch to 30 ft and fluorspar has been found in veins to depths of 900 ft in Illinois and more than 500 ft in Kentucky.

The dominant minerals in one of the typical veins in Illinois are calcite and fluorite. Other primary minerals include quartz, galena, sphalerite, pyrite, barite, and chalcopyrite; quartz, calcite, barite, gypsum, malachite, limonite and others occur as secondary minerals. In places, the fluorite content diminishes with depth and its place is taken by calcite. The vein material probably was formed through two processes of deposition: (1) vein filling and (2) replacement of brecciated calcareous vein material and wall rock.

The tabular, horizontal deposits, variously termed blanket deposits, bedded deposits, and bedding-replacement deposits, near Cave in Rock, Illinois, have attained importance in the past two decades because of the high quality of the product, the associated commercial sulphides, the relatively low cost of milling and the potential reserves. The ore outcrops just below the basal shale of the Rosiclare sandstone and dips gently to a depth that in some places exceeds 350 ft. It consists of inter-banded fluorite and sphalerite that has replaced the upper beds of the Fredonia limestone. In places, a few inches to 2 ft of coarse-grained,

massive, rather pure fluorite is found at the top of the ore bodies. The ore averages 4 ft in thickness, but thicknesses up to 12 ft are not uncommon. Vugs found in this zone have yielded many handsome aggregates of well-crystallized fluorite, sphalerite, calcite and barite. Studies made in 1937¹⁴ show that the fluorspar deposits are replacements of certain beds of limestone and are genetically related to minor fissures, of little or no displacement, that are greatly constricted or die out entirely at the ore horizon. The shale roof evidently acted as a barrier to the mineralizing solutions that traveled along these fractures and spread out beneath this impervious stratum. The Cave in Rock locality lies just east of the area of pronounced faulting wherein the vein deposits of fluorspar were formed. The mineralizing solutions may have migrated laterally from major faults and spread through minor fissures. Similar bedding-replacement deposits are known near Carrsville, Livingston County, Kentucky. The bulk of the fluorspar production from the Illinois-Kentucky field has come from the vein deposits, which have produced several million tons; the Rosiclare vein alone has yielded a large share of this tonnage. Production from the bedded deposits has become very substantial in the last decade.

WESTERN STATES

Fluorspar occurs in most of the states from the Rocky Mountains westward.^{5,23,37} Many of these occurrences are in association with other mineral deposits and are not of commercial value for fluorspar alone but commercial production of fluorspar has been reported from Arizona, California, Colorado, Idaho, Montana, Nevada, New Mexico, Texas, Utah, Washington, and Wyoming. Production from the western states during the war was greatly stimulated, reaching 30 pct of the national total in 1944, compared with a 9 pct average during the 1930s.

In Arizona, occurrences are reported in seven counties but production has come principally from Greenlee County and the Castle Dome district, Yuma County, where, accompanying galena, it occurs as a vein material in volcanic rocks.¹

Fluorspar occurs in many places in Colorado as a gangue with metalliferous ores; it has been mined for itself in seven counties, the most important of which are Boulder, Chaffee, Mineral, and Jackson. The fluorspar was first used in small quantities in refining gold and silver; the basic open-hearth steel plant at Pueblo was the first large market for Colorado fluorspar; during the war large quantities were shipped east.^{9,24}

In Nevada, the production has come from Mineral and Nye Counties.

In southwestern New Mexico, numerous deposits, most of them small, have produced fluorspar. Two types of deposits have been recognized: vein fillings in igneous and sedimentary rocks and blanket re-

placements in limestone. The veins in Sierra and Dona Ana Counties are mineralized to a depth of several hundred feet, possibly 1000 ft, and contain large reserves of fluorspar. Some of it is siliceous and requires careful ore dressing to yield a marketable product. During the recent war, Valencia County was an important producer from veins in granite; there was also production from Luna, Grant, Hidalgo, Catron, and Bernalillo Counties.⁴²

In Utah, fluorspar has been produced principally in Beaver County; a little has been reported from Juab and Tooele Counties.

During the war and previously for some localities, small production of fluorspar was reported from Riverside and San Bernardino Counties in California, Lemhi County in Idaho, Lewis and Clark County in Montana, Hudspeth and Burnet Counties in Texas, Ferry County in Washington, and Albany County in Wyoming.

Foreign Deposits of Fluorspar

Africa—Commercial fluorspar occurs in the Union of South Africa, Southwest Africa and in Tunisia.^{18,25,27} The mines are not highly developed but no doubt are adequate for most internal requirements and for some exports. South Africa exported more than 4000 tons of high-grade, hand-sorted fluorspar to the United States in 1943 and 1945.

Argentina—Fluorspar occurs at San Roque, Cordoba Province, Argentina,²⁵ in fissure veins cutting biotite gneiss country rock. The value of this district is doubtful because of its remoteness from markets.

Australia—In eastern Australia,²⁵ fluorspar occurs in veins, lodes, and vugs in sedimentary rocks, and in granite associated with silver-bearing galena and other minerals. The fluorspar, produced partly as tailings, is used locally in steelworks at Newcastle and small quantities are exported.

Canada—Fluorspar occurs in British Columbia, Ontario, the Northwest Territories, Quebec, New Brunswick, and Nova Scotia.^{16,25,45} In British Columbia, the Rock Candy deposit in the Grand Forks mining division formed a large ore shoot containing a network of replacement fluorspar veins varying from a few inches to 30 ft in width and lying within a body of syenite of Tertiary age. Fluorspar occurs in more than 100 localities north of the Great Lakes in Ontario, from Fort William eastward to Ottawa. The fluorite is associated with a large variety of vein minerals and the wall rocks range from pre-Cambrian crystallines to Paleozoic limestone and dolomite. Few of these deposits have been of commercial value. However, during both World Wars, under the stimulus of war prices, several deposits were opened and considerable fluorspar was produced.

China—Fluorspar mined by coolies in eastern China²⁵ was exported to Japan and the United States prior to the recent war. The war

and present conditions in China lead one to believe that the industry could not have prospered.

France—Fluorspar has been found in 12 French Departments²⁵ but it has been produced only in Haute Loire, Puy de Dôme, Saône et Loire, and Var. Production in some years has been substantial and mining and milling techniques are said to be advanced. No information concerning production during the last war or the present condition of the industry is available.

Germany—Fluorspar production in Germany^{25,32,36} for many years has been second only to the United States and in one year it was greater. There are workable deposits in Bavaria, Thuringia, Anhalt, Prussia, Saxony, and Baden, but the most productive mines are in the Stulln Nabburg-Woelsendorf area of Bavaria and near Rottleberode, in the Harz mountains. Virtually no war damage was suffered by the large Bavarian mines. It is estimated that their capacity now is about 150,000 tons per year, but the small reserves will not support production for many years at that rate. Before the war the operations were in strong hands and they were probably efficient. Exports to the United States are likely to be resumed.

Great Britain—Fluorspar occurs in Derbyshire, Durham, Cornwall, Devon and North Wales.^{25,34,35} The veins in Derbyshire and Durham average about 6 ft in width and the greatest length is 7 miles. They cut Carboniferous limestone and contain fluorite, barite, quartz, calcite, galena, and sphalerite. For a time the output was in excess of domestic requirements and much was exported to the United States. The mines originally were worked for lead and fluorspar was rejected. Later the fluorspar was recovered from the waste heaps but now, as these are nearly exhausted, the mineral is being recovered as a by-product of the lead-mining industry. In the Weardale district, Durham, fluorspar is the principal constituent of fissure veins cutting sandstone, shale, and limestone. In Cornwall and Devon, the fluorspar is associated with copper, lead, tin, and tungsten minerals. The famous "Blue John" fluorspar used for ornaments was obtained at Castleton, Derbyshire.

Italy—Fluorspar occurs in Lombardy, Trentino, and Venetia Provinces.²⁵ In several deposits the fluorspar is a by-product of silver-bearing galena ores, as at the Rabenstein mine in Trentino. Italian production and reserves are not large but probably they will meet domestic requirements. Information concerning the industry during and since the war is unavailable but probably it is active now; up to mid-1948, four post-war shipments had been made to this country, totaling 6489 tons. This was the first European fluorspar other than that from Spain to be imported into the United States since before the war.

Mexico—The principal fluorspar deposits of Mexico^{20,25} are in the

states of Chihuahua, Durango, and Guerrero; less important ones are in northern Sonora; near Muzguiz, Coahuila; in Mexico; Hidalgo, and Guanajuato.

The two largest producing mines are in the state of Guerrero, near Taxco; reserves in this district are large and the fluorspar is free milling and high grade. Probably the largest single reserve is near Parral, in Chihuahua, but the ore is siliceous and difficult to concentrate. Other important deposits are near Bermejillo, Rosario, and Guatimapé, all in Durango, and near Jiminez in Chihuahua.

Most of the Mexican fluorspar production during the war and subsequently has been produced by simple means involving much hand labor and little machinery; the bulk of the tonnage has come from surface workings and was hand-sorted or gravity-milled to yield a marketable product.

Undoubtedly Mexican reserves are large; and, since her domestic requirements are small and production costs are low, considerable exports to the United States seem probable in spite of high freight rates. Since the war, our imports from this country have averaged in excess of 3000 tons per month, much more than all other imports combined.

Newfoundland—Fluorspar from Newfoundland^{25,26,44} comes entirely from the St. Lawrence district. Steeply dipping, epithermal veins occur in granite, rhyolite porphyry, and lamprophyre, and vary in grade from 75 to 95 pct fluorite and in thickness from 5 to 20 ft; quartz, calcite, some barite, pyrite, chalcopyrite, galena, and sphalerite are the usual associated minerals. During the war, a large tonnage was produced by the two principal operators, and it is likely that Newfoundland will play a substantial role in future world production. Reserves are believed to be large.

Russia—Russian^{25,30} reserves of fluorspar of commercial grade are probably large but the great distances between deposits and markets, and the poorly developed transport system, no doubt will cause many of the large deposits to remain undeveloped for many years. Geologically the deposits evidently are as varied as those of the United States. Deposits of importance are reported in Eastern Transbaikalia, in Tadjikistan, and Kazakhstan, in the Urals, and in the Far East. The latter have received relatively little attention because of their remoteness from markets.

Spain—The most important Spanish fluorspar mines^{4,25} are in Asturias, near Gijon and Ribadesella; less important ones are in the districts of Cordoba, Barcelona, and Gerona. Reserves are not large but Spain should be able to more than satisfy its domestic needs. Normal prewar production averaged 8000 tons per year but in 1944 more than 51,000 tons was produced, much of it no doubt for use in German

industry. During the war, a total of 49,768 tons was purchased by the United States Government as a part of its preclusive purchasing activities.

POLITICAL AND COMMERCIAL CONTROL OF FLUORSPAR

Fluorspar is highly important, and in many cases indispensable, to so many basic industries such as steel, aluminum, chemical, and ceramic, that in time of war or threat of war, no nation could consider itself industrially strong without adequate internal production or secure sources of adequate imports. Germany, historically the world's second largest producer, cut off all exports prior to World War II, and the United States, though the largest producer, was sorely pressed early in the war to meet the demand. Reserves in the United States are large, however, and domestic production under the stimulus of higher prices was adequate in both wars to meet all requirements. As in World War I, imports were greatly reduced with the outbreak of the recent war, but by 1943 they began again to flow in important quantities, from newly developed sources in some cases.

Throughout the war, the country was faced with unprecedented demand and it became necessary for the Government to assure even distribution of consumer inventories, to liberalize specifications, and to promote conservation. Prices and wages were controlled, but otherwise Government control of the industry was mild; and by late 1944, with expanded domestic production and imports, most controls other than those over prices and wages were relaxed or abandoned. In other ways the Government strove to bring supply into line with demand. The United States Geological Survey studied and reported upon a very large number of potentially productive areas and the Bureau of Mines drilled and otherwise prospected some of those with most promise. Additionally, the Bureau of Mines performed valuable service to the industry and to the war agencies, beginning early in 1942, by collecting and publishing monthly statistics on production, consumption, and stocks. These figures are still being compiled and may be obtained by writing to the Bureau.

The Reconstruction Finance Corporation, through its subsidiary agencies, built or financed a number of concentrating plants and made purchase contracts to encourage production. The purchase contracts were terminated in 1945 and the last Government operation, at Gila, New Mexico, was shut down in May 1947. To keep production and imports at high levels, to meet any possible unforeseen new demand, and to reduce the effects that a major flood in the Ohio River might have on production in Illinois and Kentucky, the Metals Reserve Co. began in 1943 to form a Government stock pile, which in 1945 reached a maximum of 245,728 tons. Some of the Metals Reserve stock pile of both

metallurgical and acid grade was consumed at a time of stringency in the supply. What remained was transferred after the war to the Bureau of Federal Supply as a permanent stock pile; these figures are not published. Part of the stock-piled tonnage resulted from the Government's preclusion purchasing activities in Spain; the rest was acquired from Mexico, Newfoundland, the Union of South Africa, and domestic sources.

In the steel industry voluntary conservation effectively reduced consumption from a high in 1942 of 6.4 lb per ton of basic open-hearth steel to a low of 5.5 lb in 1945. Attempts were made to find substitutes; but, although many were tried, none proved nearly as effective as fluorspar.

Two price advances were authorized by the Office of Price Administration; the second, on July 1, 1943, was accompanied by a wage advance in Illinois and Kentucky, which averaged 24 pct. Increased production resulting from an improved labor supply was noticeable.

In 1942, Congress passed temporary legislation putting the industry on virtually the same basis as regards percentage depletion as the metal mining industry. In August 1947, permanent legislation to this effect was enacted.

Since 1937, two changes have been made in tariff rates: On Jan. 1, 1939, by agreement with the United Kingdom, the rate on the high grade (over 97 pct fluorite) was reduced from \$5.60 to \$4.20 per long ton; on Jan. 30, 1943, the tariff on the low grade (under 97 pct fluorite) was reduced from \$8.40 to \$6.30 per long ton. During 1947, the Government was considering further reductions, which the industry concertedly protested. The foregoing rates were still applicable in November 1948.

From 1923 to 1938 imports averaged 25 pct of the total supply. What they will be under normal postwar conditions is difficult to foresee but, with the lower tariffs and deflated currencies, it seems possible that they will be larger. Newfoundland and Mexico became important producers during the war and Germany and Spain are likely again to export considerable tonnages to this country.

Most of the world's great powers and some of its minor ones possess reserves of fluorspar that are adequate for peace and wartime needs. Most of the deposits, except probably for those in the totalitarian communist countries of eastern Europe and Russia, are in private hands. However, many deposits are small, requiring relatively little capital by comparison with that required in copper or iron mining or in the petroleum industry; consequently, even in the totalitarian states some degree of private control may exist.

Reserves in the United States, like our reserves of other neutral resources, were given serious study during the war years; for 35 pct of

our all-time production was shipped³⁸ between 1939 and 1945. Measured, indicated, and inferred reserves, most of which are in the Illinois-Kentucky field, were estimated at the beginning of 1944 at 9,000,000 tons, including 1,700,000 tons from presently noncommercial ores carrying 15 to 35 pct fluorite. This is about 55 years supply at the 1935-1939 average rate of consumption. Tonnage has been mined since that period at a much higher average rate and it is reasonable to assume that consumption in the future will considerably exceed the 1935-1939 average. Assuming no imports, it might be presumed therefore that we now have roughly 35 years of total reserves including low-grade, presently noncommercial ores. But new discoveries, new processes for treating hitherto refractory ores, imports, and higher prices will almost surely result in substantial production, perhaps even self-sufficiency, for additional years. Higher prices will come as the need for working lower-grade deposits increases, and it is significant that the cost of fluorspar is an almost insignificant part of the cost of steel, aluminum, and the other products made with or from it.

As fluorspar has grown in commercial importance, there has been a marked tendency for consuming companies to assure their supplies by long-term contracts and by the acquisition of interests in producing or potentially productive properties. This has resulted in some concentration of production in fewer and stronger hands. Nevertheless, no one producer normally ships more than 15 pct of the total, and it required 10 operations to produce barely half the total product in 1945. In that year, 63 mines produced 95 pct of the total.

PRODUCTION AND CONSUMPTION OF FLUORSPAR

An interesting outline of the history of production of fluorspar has been prepared by Hatmaker and Davis, from which many of the following facts are derived:²⁵

Agricola (1529) considered fluorspar a highly useful fluxing agent but its extensive use did not develop until just before the beginning of the twentieth century. Discoveries of fluorspar, or "fluete of lime," were recorded in 1814-1816 near Franklin Furnace and Hamburg, New Jersey, and in other eastern and New England states; the occurrences in southern Illinois were reported as early as 1818 and deposits in Tennessee and Kentucky a few years later. Fluorspar was recorded in Colorado in the late '60s and in New Mexico, Arizona, and other western states soon afterward. The first recorded use of American fluorspar apparently was in 1823, when 2 oz of pure fluorspar from Shawneetown, Illinois, were used, with 4 oz of sulphuric acid, in making fluoric acid. In 1837, fluorspar mined from a vein near Trumbull, Connecticut, was used with magnetic iron pyrite in the smelting of copper ores.

Mining fluorspar in southern Illinois began near Rosiclare in 1842;

shipments apparently began about 1870, in Kentucky about 1873, and in Colorado in the early '70s. The principal uses of fluorspar up to 1887 were in the manufacture of glass, enamels, and hydrofluoric acid; smaller quantities were used as a flux in iron foundries and in smelting gold, silver, copper, and lead ores. At this time the annual requirements were about 5000 short tons, and about 1888, with the commercial manufacture of basic open-hearth steel in the United States, the production of fluorspar began to increase.

With the rapid increase in the production of open-hearth steel, together with increases in the demand from the ceramic and chemical industries, the consumption of fluorspar rapidly multiplied. The high for any prewar peacetime year was 218,500 tons (in 1940), but this figure was exceeded in 1918 and nearly doubled in 1944, when 410,000 tons was consumed. The total production of fluorspar in the United States from early in the nineteenth century through mid-1948 has exceeded 7 million short tons, of which Illinois and Kentucky have contributed approximately 53 and 34 pct, respectively. Colorado and New Mexico in that order have produced most of the remaining 13 pct.

Domestic consumption of fluorspar for the period 1935 to 1939 inclusive, which is perhaps a normal prewar period, exceeded production by less than 10 pct. In the '20s and early '30s the figure was very much larger. The United Kingdom during most of the '20s was the principal foreign source, but from 1927 through 1938, Germany held the lead with France, Italy, and Spain supplying lesser tonnages. During World War II, Mexico was the principal foreign source. Consumption during the period from 1935 to 1939 ranged from 115,000 to 194,000 tons annually and averaged 161,000 tons. During the war years, the average was approximately 364,000 tons. Domestic production during the prewar years never supplied less than 59 pct of the total consumed in any one year and during the 1935 to 1939 period it supplied an average of 87 pct. Consumer and producer stocks normally have amounted to about eight months' requirements, the bulk being in the hands of consumers. During the last war, however, there were periods when total inventories were less than four months' requirements. Exports have never been significant.

Fig 1 shows domestic production, consumption, stocks, imports, exports, and average prices of fluorspar in the United States for the period 1929 to 1947, inclusive.

Statistics for production of fluorspar in foreign countries are not complete, particularly in recent years; however, what is available has been well presented in the recent Minerals Yearbook. Fig 2 sets forth in graphic form the information available from that source. In most years, the United States has been the leading producer and in some years has produced more than half the world's total.

During the period 1933 to 1935, inclusive, the mines in Illinois produced 0.48 ton of finished product per man-shift; for those in Kentucky, the figure was 0.37 and for the United States as a whole, the figure was approximately 0.43.

EXPLORATION, PROSPECTING AND MINING OF FLUORSPAR

Methods of prospecting and exploration for fluor spar deposits parallel those for many other mineral deposits; they vary according to the region and type of deposit concerned. Primary guides for prospecting are surface indications. In the Illinois-Kentucky district, the outcrop of a vein is marked in places by the presence of gravel fluor spar in the soil or subsoil. A fault fissure is indicated by rocks of unlike character in contact along a horizontal plane and may be marked, for example, by a ridge or low bluff of sandstone that has resisted weathering more than the limestone or shale on the other side of the fault, or by a sharp difference in the soils. In the West, where fluor spar may be an abundant gangue mineral, fluor spar float, or even fluor spar sand brought up in anthills, may indicate the presence of veins. In Illinois and Kentucky, geophysical surveys designed to detect the presence of concealed faults have been made. This work, carried on in 1933 to 1935 by the Illinois State Geological Survey and the United States Geological Survey, employed electrical resistivity methods to indicate abrupt transitions between beds of different resistivity that had been brought into juxtaposition through faulting. These methods did not prove particularly successful.

Known or suspected fault fissures are prospected for fluor spar values by standard methods such as trenching, test-pitting, sinking shallow shafts, churn drilling, and diamond drilling both from the surface and underground. In prospecting for bedding deposits remote from outcrops, churn drilling has proved most practicable.

Progress in prospecting techniques during the past 10 years has largely been in the development of better core-drilling equipment and in the fuller study and application of geology.

Fluor spar deposits, to be commercial, must, like any other mineral deposit, be capable of production at a cost that will yield a profit margin commensurate with the risk. Such matters as structure, attitude and width of vein, grade and character of the fluor spar, identity and character of the associated minerals, distance to railroad and markets, cost of mining and processing, capital requirements, water supply, to name some of the most important factors, must be considered. In general, it has been possible in the past to undertake to mine fluor spar ores with relatively small amounts of capital. However, the easy-to-find, cheap-to-operate deposit is becoming scarcer, and in the future new enterprises will require more capital than heretofore.

As with the mining of any mineral deposit, the methods employed in mining fluorspar in the United States vary according to the nature of the deposits and the technical and financial ability of their proprietors. Many failures, as in all mining ventures, have been due to lack of careful consideration of all pertinent information and circumstances, and to undue haste to attain immediate production. Fluorspar mining, whether of steeply dipping veins or of flat-lying lens-shaped beds, is in all essential respects similar to the mining of small to moderate-sized metalliferous deposits. Mining is done most commonly by the regular underground methods but small opencuts and glory holes have produced small tonnages. Where the disintegrated material on the weathered outcrop of a vein contains valuable fluorspar in the form of residual gravel or lumps, it is mined from open pits by simple hand methods or by steam shovel. This type of deposit is now of very minor importance.

The bedding deposits of fluorspar at certain mines near Cave in Rock, Illinois, crop out above the general level of the surrounding country and are reached by shafts or adits. Where of workable thickness (usually more than 3 ft), the ore is extracted by a modified room-and-pillar method. Access by means of adits is also applicable to vein deposits in regions of rugged topography where the veins dip steeply and rise high above drainage.

The mining practice of several of the larger, more substantial companies has been fully described in the literature.^{11,28} Shrinkage and top slicing are methods commonly employed. Little change has taken place in methods during the last decade, except for more mechanization involving the use of mucking machines, slushers, mechanical haulage, and other equipment. The most serious problem in the shaft mines on the Rosiclare vein in Illinois is that of handling the large quantity of water that enters the mines through channels in the limestone and from the Ohio River where it intersects the vein. The principal mines have been flooded repeatedly.

PREPARATION OF FLUORSPAR FOR MARKET

Fluorspar ore as it is mined contains other minerals besides fluorite and usually it is diluted with country rock. The methods of treatment depend upon the nature, quantity and character of the fluorspar and of the associated impurities, and upon the use that is to be made of the final product. A very few small deposits contain such pure ore that hand cobbing and sorting yields marketable lump ore. The impurities commonly associated with fluorspar in Illinois and Kentucky are calcite, quartz, clay, and sand, together with wall rocks such as sandstone, shale, and limestone, none of which are especially harmful except as diluents. But the ores often include also barite, galena, sphalerite,

pyrite, and other compounds of lead, zinc, and iron, which even in small quantities may cause a product to be unmarketable. The sulphides are sometimes in sufficient quantity to be of commercial value and to warrant recovery. In the western states, the same impurities often are present as well as other metallic and nonmetallic minerals and different wall rocks such as granite, andesite and rhyolite.

The methods of separation are the standard ore-dressing techniques based on gravity differences, naturally occurring size differences, visual differences, and on characteristics permitting differential flotation; they include hand sorting, washing, screening, gravity separation by jigs and tables and latterly in heavy-media equipment, and flotation. The processes may be very simple: residual gravel deposits may be crushed, washed, and screened to produce a satisfactory gravel fluorspar for use as a flux in open-hearth steelmaking; or they may be very complicated, as in the preparation of complex, finely intergrown ores for the ceramic trade or for acidmaking. The milling of fluorspar for the ceramic or acid trade is relatively more difficult and requires more careful control than do the heavy metal ores. Much more rigid specifications must be met.

No new techniques have been developed during the past 10 years but there have been improvements in the old techniques, such as the use of improved flotation reagents and heated flotation circuits. Also, the heavy-media principle has been successfully applied in several large mills, and it is proving to be an effective means of increasing recovery and grade cheaply. In at least one mill, metallurgical "gravel" fluorspar is being made from finely ground flotation concentrates by pelletizing with tall oil as a binder. The product is satisfactory to steelmakers but is not as resistant to weather and abrasion as is the standard gravel. Very considerable research has gone into the development of a satisfactory pellet and pelletizing should not be counted upon as a means for marketing a lot of off-grade acid fluorspar. Dry tabling and decrepitation have been tried with little success. Mill capacities vary from a few tons of ore per day to many tons per hour.

A large and complete concentrator producing perhaps two or three fluorspar products by flotation, together with a lead and zinc concentrate, will cost several hundred thousand dollars even at prewar prices, considerably more per daily ton of capacity than the cost of concentrators for the heavy metals.

Attention should be drawn to the trend toward more complicated milling techniques as the easily concentrated ores become exhausted. This is illustrated by the considerable production of metallurgical gravel by flotation and pelletizing during the war. It results in part from the increasing relative demand from the chemical industry, which

requires great purity and a finely ground product. Several fluorspar concentrators have been fully and well described in the literature.^{8,10,17,28}

TESTS AND SPECIFICATIONS FOR FLUORSPAR

In order of their importance from a tonnage standpoint, there are three principal commercial grades of fluorspar. The first is the metallurgical grade used almost exclusively in the basic open-hearth and basic electric steel industry. About 55 pct of total consumption is of this grade. Chemically this product should contain not less than 85 pct fluorite and not more than 5 pct silica and 0.03 pct sulphur. These specifications were considerably relaxed during the war (with probably little or no damage to the steel industry). In the western United States, where silica is the predominant associate mineral in the ores, a lower fluorite content and higher silica content is accepted. Physically, metallurgical gravel must pass a 1-in. screen and must contain less than 15 pct fines. Lump metallurgical fluorspar, known as No. 2 lump, from 2 to 6 in. in diameter, is used as a flux in foundries making high-grade iron castings.

Acid-grade fluorspar, constituting about 28 pct of the total post-war production, must contain not less than 98 pct fluorite nor more than 1 pct silica. Barite, lead, zinc, lime, and iron also are unwanted impurities because they interfere with the making of hydrofluoric acid. The fluorspar must be finely ground and must be absolutely dry. Under wartime conditions, and to bring refractory ores into the market, specifications were slightly relaxed. Some lump acid-grade fluorspar is sold as No. 1 lump but the tonnage is very small.

Constituting about 15 pct of the total product, the ceramic grade is an intermediate one chemically. A minimum of 95 pct fluorite usually is required and 2.5 pct silica is the standard maximum. It must be colorless and therefore can contain not more than 0.12 pct ferric oxide and only traces of other iron compounds or lead or zinc sulphide. These specifications may be considerably modified for some uses.

Optical fluorite is an important minor product, which must be absolutely clear, free of cloudiness or inclusions, cracks or cleavage marks. It can have slight color. To be commercial, a rough piece must be large enough to allow a clear piece $\frac{1}{2}$ in. in diameter to be cut from it. The standard method of chemical analysis for fluorspar is known as the Bidel method. A newer method known as the Willard-Winter gives direct fluorine determinations and is superior and faster for some purposes.

MARKETING AND USES OF FLUORSPAR

The bulk of the fluorspar marketed in the United States, and most of that imported, is used in the steel industry, principally in the basic

open-hearth process, in which it is added as a flux to the furnace charge to give fluidity to the slag and to facilitate the passage of objectionable impurities, such as sulphur and phosphorus, into the slag.²⁸ Fluorspar is known to possess considerably higher quantitative efficiency as a flux than limestone, especially in the smelting of refractory ores, but in all metallurgical operations the proportion that can be used is limited, since its favorable effects do not increase indefinitely as the quantity is increased. The quantity of fluorspar used per ton of basic open-hearth steel varies widely between plants; a normal average is about 6.5 lb per ton. Since fluorspar is not a costly product, it is a relatively small item in the cost of manufacturing a ton of steel. It is used as a flux to make ferroalloys, nickel, brass, basic refractories, and bessemer steel. It is also used to refine several of the nonferrous metals.

The acid grade of fluorspar is used almost exclusively to make hydrofluoric acid by reaction with sulphuric acid.^{6,19,21,31,40} This is the first step in the manufacture of numerous products, the most important of which is artificial cryolite, the electrolyte used to reduce aluminum from its oxide. Fluorine chemistry seems to be on the threshold of considerable growth, and many relatively new products based on hydrofluoric acid are being marketed. One of the most important is an organic compound called Freon 12, used extensively as a refrigerant and as a carrier known as Aerosol for certain insecticides. Hydrofluoric acid is used to make high-octane gasoline and was used during the war in the manufacture of the atom bomb. It is being used to make numerous organic and inorganic fluorine compounds, in the etching of glass, and to make the element fluorine. The acid grade also has some fluxing uses. An interesting new use of a fluorine compound is in the production with oxygen of a very hot cutting flame.

In the ceramic industry, fluorspar is of value in the manufacture of opalescent, opaque, and colored glass, enamels, facings for bricks and Vitrolite, and in the manufacture of portland cement. It is also used as a bonding agent for the constituents of emery wheels, in the manufacture of carbon electrodes, and in the preparation of electric-arc welding electrodes, where the fluorspar serves as a flux.

A very small quantity of optical-quality fluorspar is used to correct the color and spherical aberration errors in lenses of microscopes and small telescopes.³⁹ Artificial lithium fluoride, a product of acid-grade fluorspar, is being used for similar purposes.

An outline of marketing practice is as follows:²⁵ Prices of domestic fluorspar are quoted on the basis of the short ton f.o.b. cars or Ohio River barges at the nearest shipping point to mills or mines. Gravel and lump fluorspar are generally shipped in bulk in open-top cars. Ground fluorspar is shipped (1) in bulk in boxcars lined with heavy paper, (2) in bags with a capacity of 125 lb, (3) in barrels with a capacity of from

450 to 500 lb, or (4) in bulk in special railroad cars designed for the purpose.

Most of the large consumers buy their fluorspar on contract, generally covering a definite tonnage to be delivered within a stated time and specifying the minimum content of calcium fluoride and the maximum content of the various impurities that will be accepted. The contract may or may not include penalties for excessive impurities above the specified limits. Premiums, however, are seldom paid for unusual purity.

Most of the domestic fluorspar of commerce is sold through established sales agencies that handle other raw materials used in the iron, steel, ceramic, and chemical industries and are thus in close contact with consumers. Occasionally, such sales agencies have operated their own mines but more frequently they contract with producers for their entire output. The usual commission for such services is 5 pct of the f.o.b. value.

The cost of production and transportation limits the markets in which sellers of fluorspar can profitably compete; these factors and the import duty limit the market for foreign fluorspar. The cost before the war of producing fluorspar abroad, chiefly in England, Germany, and France, was relatively much lower than the cost of production in the Illinois-Kentucky district. Hence, notwithstanding the duty, fluorspar imported from these sources was sold in western Pennsylvania and to a small extent in eastern Ohio in stiff competition with that from the Illinois-Kentucky district. The market in this wide seaboard area was therefore more or less divided between domestic and imported fluorspar. It is difficult to say what the competitive position of the domestic industry will be under normal postwar conditions; but with the duty on fluorspar lower than before the war, with new and important deposits developed in Mexico and Newfoundland, and with higher world prices, it is likely to be somewhat less good than before the war. Indications in 1947 and 1948 bear out this conclusion.

PRICE HISTORY OF FLUORSPAR

Historical data on fluorspar prices can best be obtained from the Minerals Yearbooks. Current price information is published in technical and trade journals.

Prior to the entrance of the United States into World War I, or from 1880 to 1916 inclusive, the average f.o.b. price of all grades of fluorspar was comparatively uniform, ranging from about \$4.00 to \$8.21, and averaging \$6.07 per short ton. In 1919, the price reached \$25.49 but in the following 20 years the average price for all domestic fluorspar was \$18.41, ranging between \$14.25 and \$21.00 per ton. During this period a differential began to develop between the prices for

acid, ceramic, and metallurgical fluorspar; the acid and ceramic grades commanded a premium of several dollars. With the advent of World War II, prices began again to rise until they were curbed in 1941 by Office of Price Administration ceilings. On July 1, 1943, revised ceilings were placed in effect: i.e., \$30 to \$33 for the metallurgical grade, depending on its fluorite content, and \$37 for both the acid and ceramic grades. (The \$33 price for metallurgical fluorspar was for material meeting prewar standard specifications.)

The average prices in 1944 and 1945 under the OPA were \$30.22 and \$30.55; with ceilings removed in 1946, the average was \$32.52, all per short ton f.o.b. mine or mill shipping points. The increase in price in 1946 did not result significantly from the removal of ceiling prices; rather, it resulted from increasing shipments, proportionately, of acid and ceramic grade and from the shipment of proportionately less substandard metallurgical grade. The average price in 1947 was \$33.25. Western mines are generally handicapped by the freight differential, and these differentials were recognized in the OPA ceilings.

The industry is keenly competitive and it can truly be said that the demand of the steel industry and the cost and supply of Illinois-Kentucky fluorspar in competition with imports largely determines the price for the metallurgical product.

Before and during World War II, under OPA ceilings, the differential between acid fluorspar and standard metallurgical gravel was about \$4 per ton. The differential is likely to be larger in the future because of the relatively greater demand for the high grade. In 1947, it was \$11.84. The differential during the war was actually about \$6.75 because much substandard metallurgical material was shipped. The quality of deliveries has tended to improve since the war. Average prices since 1929 are portrayed graphically in Fig 1.

CRYOLITE

Cryolite is a double fluoride of aluminum and sodium ($3\text{NaF} \cdot \text{AlF}_3$), which when pure contains 12.8 pct aluminum, 32.9 pct sodium and 54.3 pct fluorine. It crystallizes in the monoclinic system; its hardness is 2.5, specific gravity 2.96, and the pure mineral is colorless. The ore is often dark in color because of contamination with fluorite, quartz, chalcopyrite, pyrite, siderite, galena, sphalerite, and other minerals. The mineral fuses at 950°C with practically no loss in firing. It is very slightly soluble in water. The mineral is comparatively rare. Its only important commercial occurrence is at Ivigtut, Greenland. Very small, commercially unimportant occurrences are known in the St. Peter's Dome district, Colorado; at Miask, in the Urals and in Canada.⁴⁶⁻⁴⁸

At Ivigtut the cryolite ore is associated with pegmatite within an intrusive mass of porphyritic granite. It lies on the shore of Arsuk

Fjord, conveniently situated for mining and shipping the product. The mine is worked from slopes leading from the bottom of an open quarry about 500 ft long, 300 to 600 ft wide and 150 ft deep.

The mine is owned by the Danish State and the mining concession by the Kryolitselskabet Oresund A/D, Copenhagen. The crude ore output is normally divided about equally between the Pennsylvania Salt

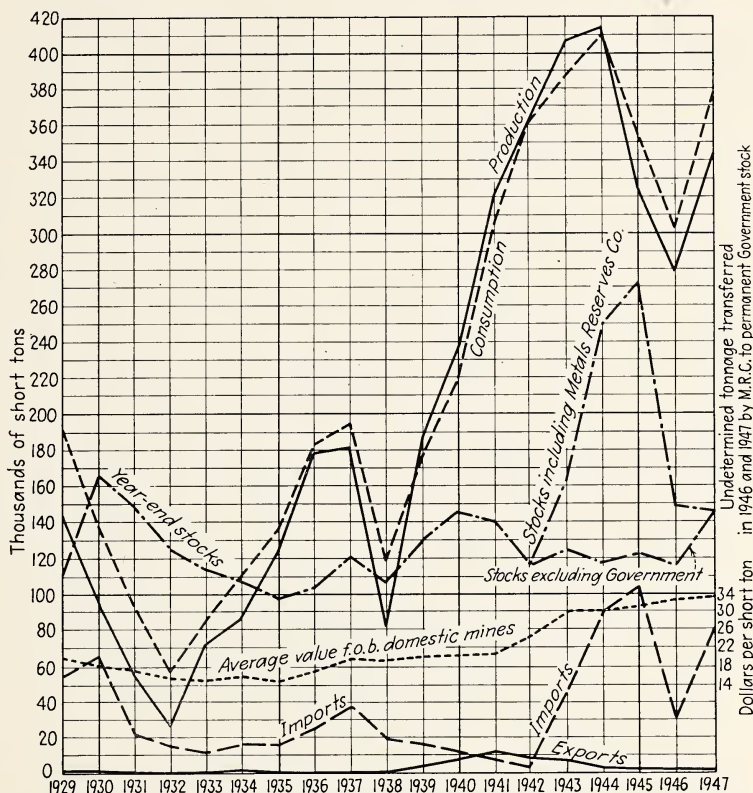


FIG 1—TRENDS IN PRODUCTION, CONSUMPTION, STOCKS, IMPORTS AND EXPORTS OF FLUORSPAR IN THE UNITED STATES AND AVERAGE VALUE F.O.B. DOMESTIC MINES, 1929-1947.

Manufacturing Co., of Philadelphia, and the Danish company's manufacturing plant in Copenhagen.

The crude ore, as mined and containing silica, fluorspar, galena, pyrite, siderite and host rock gangue, is shipped as is to the Pennsylvania Salt Manufacturing Company's processing plant near Pittsburgh, where it is converted into various manufactured products. Prior to 1935, separation of the ore was mainly effected by gravity, but since that time flotation and other mineral-dressing techniques have been employed to better meet rigid product specifications.

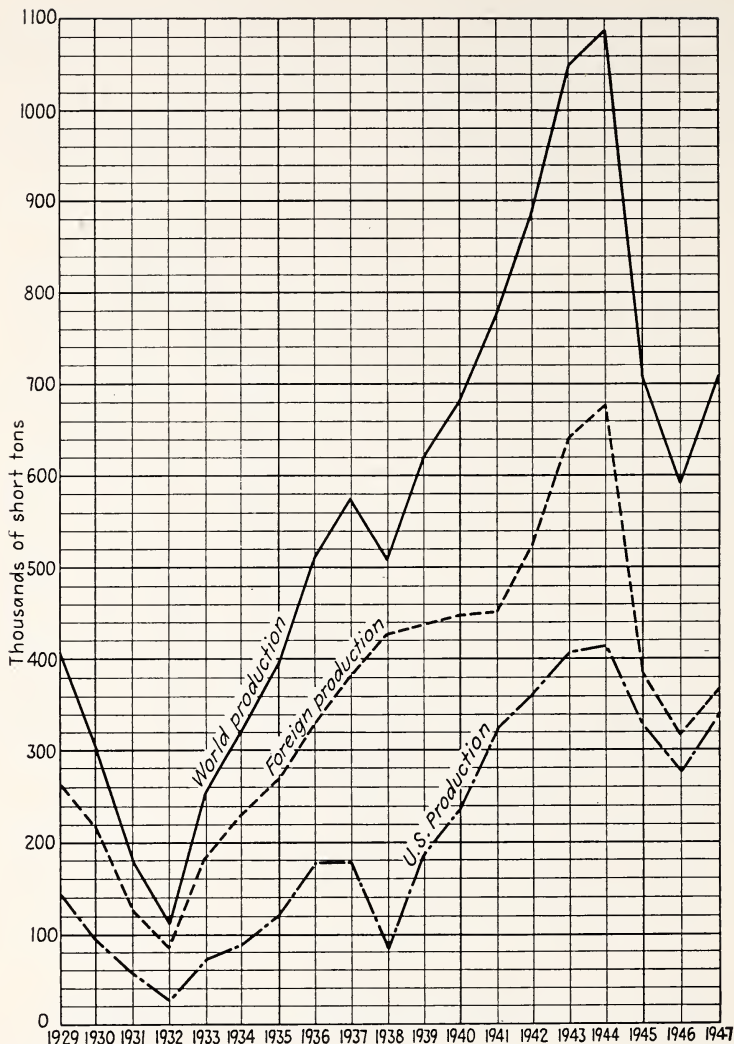


FIG 2--TRENDS IN PRODUCTION OF FLUORSPAR, WORLD, FOREIGN COUNTRIES AND UNITED STATES, 1929-1947.

Foreign production in part estimated by the Bureau of Mines.

The flotation concentrate is a finely divided white powder typically containing 99.4 pct natural cryolite. The principal use for this product is in the aluminum industry, where it acts as the electrolyte in reducing alumina to the metal. Artificial cryolite made from fluorspar is used extensively for the same purpose but it has the disadvantage of liberating fluorine-containing gases more readily than the natural product when electrolysis is started, thus causing undesirable working conditions. In the aluminum industry, iron and silica are undesirable impurities.

A high-quality cryolite product is used in the enamel and glass industry. It gives whiteness to enamel and is an opacifier in glass. Here contamination with iron impurities in any form is to be avoided.

Small tonnages are used as a binder for some abrasives and also as insulating material having special dielectric properties.

Some flotation middlings are mixed with rough-dressed ore and then dry-ground to an extremely fine powder, all below 5 microns in size and containing 90 pct natural cryolite. This product is further processed in various ways and is used exclusively as an insecticide. Natural cryolite, the active ingredient, may be applied to most crops without fear of "burning" and consequent injury to plants. The product usually is mixed with other selective insecticides and wetting or dispersing agents. All such products are proprietary compounds of the Pennsylvania Salt Manufacturing Co. Gangue impurities in these grades merely act as diluents.

The exports (equivalent to production) of cryolite from Greenland from 1935 to 1938 averaged 29,300 metric tons annually, about one half of it being shipped to the United States; during the war years, 1940 to 1944, production averaged nearly 51,600 metric tons and about 75 pct was received in this country.

The average sales price to customers of the high-quality flotation concentrate in the United States during the two periods was 8.75¢ and 10.0¢ per pound, respectively.

Imports of cryolite are set forth in the Minerals Yearbooks. Except for relatively small quantities of artificial cryolite from European manufacturers, all of it is from Greenland.

From September 1942 to October 1944, cryolite was under strict allocation by the Government. There is no tariff.

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CHAPTER 18

GRANULES

By G. W. JOSEPHSON*

GRANULAR mineral products used primarily to form a protective and decorative coating on the weather surface of composition roofing are called "granules," "roofing granules," or "slate." The latter term is a relic of the early days of the industry, when crushed slate was the dominant type of granule in use.

Asphalt roofing is made by saturating and then coating a continuous strip of felt with specially compounded asphalts. Granules are embedded in the hot asphalt on the top of the sheet, and mica or talc is dusted on the back. After passing through press rolls, the strip is looped on a conveyor for cooling and then cut into shingles or packaged as roll roofing.

HISTORICAL DEVELOPMENT

Although the durability and protective qualities of asphalt and tar have been known since the earliest days of recorded history, it was not until 1780 that the first forerunner of present-day composition roofing was developed.¹ Large-scale expansion of the industry has taken place since 1900.

At first the process consisted simply of dipping sheets of burlap or other fabric into a tank of molten tar or asphalt. The long strip of roofing was rolled up, for convenient handling, and the early experimenters soon found that it was necessary to dust the surface of their new "roll roofing" with some kind of material that would prevent the tarred surfaces from sticking together. Any finely divided, low-priced local material like sand or fine gravel served this purpose and from its application the roofing-granule industry grew.

As time went on, other characteristics of a properly applied mineral surfacing were recognized. As with wooden shingles, tar and asphalt can be ignited by flying embers from near-by fires. It was found that by increasing the largest particle size to the maximum that could be successfully embedded and by properly controlling the amount of smaller fractions retained in the grade, so as to cover the asphalt completely, a high degree of resistance to fire was attained.

* Chief, Nonmetal Economics Branch, Bureau of Mines, Washington, D. C.

When asphalt is protected from the sun's rays it is extremely durable but when exposed to sunlight its surface is comparatively rapidly decomposed. Completely covering asphalt roofing with mineral surfacing protects the asphalt and adds materially to the life of the roof—conservatively 500 pct.

In the production of split-slate shingles, a large quantity of waste slate is accumulated, as 60 to 90 pct of the rock quarried is discarded. Some of the discard was marketed as ground slate flour, for filler in paint and linoleum, and there is a record that, as early as 1906, two carloads of coarse screenings from slate flour were marketed as granules for surfacing roofing.

Slate granules had several advantages over the sand, feldspar chips, and slag that were in common use. These materials had little or no color whereas slate was available in various shades of red, green, blue-black, and purple. These natural granules were not strongly colored by present standards, but they represented a distinct step forward, which allowed asphalt roofing to rank in color with competitive materials and to be associated in name with slate, which had a long and respected history as a roofing material. The naturally good adhesion of slate granules to asphalt, its flat grain shape, which covers well, comparative freedom from disintegration, and the establishment of suppliers capable of furnishing ample quantities of reasonably uniform quality were other advantages gained. The term has become so intimately identified with roofing granules that even today, when the large percentage is made from other materials, they are known to the industry as "slate."

During the time that slate granules were gaining wide acceptance in this market, the convenient and decorative shingle form of asphalt roofing was beginning to appear.⁶ Equipped with sales advantages in fire resistance, durability, color, design, light weight, ease of application, and price, the asphalt-roofing industry made such rapid strides that by 1920 it was consuming more than 300,000 tons of granules a year.

Greenstone, colored by epidote and chlorite, was introduced as an improvement over the slate greens and achieved considerable success. A large tonnage is produced today in Pennsylvania, Michigan, and Wisconsin. Most of it serves as base rock for artificially colored granules, but some is marketed in the natural condition.

Blast-furnace slag attracted the attention of various investigators because it was available in large quantities at low prices in convenient locations. In 1914, S. W. Osgood produced the first artificially colored granules by running molten slag into solutions of sodium and potassium silicate, dusting the coated granules with iron or chrome oxide

pigment, and heating them until the coating absorbed the color.² G. S. Finney and other later experimenters have used various slags, but only a small tonnage of slag-base granules is produced today.

Naturally colored siliceous gravel has been used since before 1900 and continues to serve a limited market.

Painted granules were introduced during the first World War in response to a demand for camouflage. Many types of materials, such as slag, slate and gravel, were coated with paint in a mixer and then air-dried or baked. The paints were not sufficiently durable for use on roofing because they faded rapidly or peeled and after a few years painted granules virtually disappeared from the market.

Finney produced glass granules in 1921 by fusing limestone and quartz and by fusing slags with quartz. These granules were attractive in many ways, but very few ever were used on roofing because of their transparency, brittleness, poor adhesion to asphalt, and high cost.²

During the 1920s, Fisher developed a number of methods of coating and coloring slate. Colors ranging from red to yellow were produced by saturating the granules with sulphates of iron and copper and burning them at about 1300°F. Later, higher temperatures, around 1800°F, were tried, giving an incipient fusion of the slate.² About 1924, Fisher produced the first of his "silicate" types. The raw granules were coated with a sodium silicate solution containing suspended or dissolved compounds that act as pigments or glaze constituents.

Formulas of the silicate type have been and are now widely used on a variety of base materials. Individual producers have introduced improvements suitable to their local conditions. By adding clays or other more active materials, sodium silicate can be made reasonably insoluble at relatively low temperatures. This practice is advantageous from the standpoint of production costs and allows a wider selection of pigments, many of which cannot stand high temperatures.

Talc and pyrophyllite granules were produced by Alton in 1927 by vitrification at 2200°F. Colors were obtained by later glazing on a colored oxide. In most ways this was a satisfactory granule, but high costs discouraged development.²

Variations of a process that was introduced by G. H. Brown in 1925 have been used in the production of large tonnages of granules. Essentially it consists of coating raw granules of very refractory, siliceous rocks, like quartzite, with a solution or slurry of glaze chemicals (borax, soda ash, lime) and pigments (sodium dichromate, iron oxide, ferrous sulphate). When these granules are fired at high temperatures, up to 2500°F, metal oxide pigments are formed in a glaze that derives its silica from the granule surface. Temperatures are below the melting point of the granule, so it retains its shape. Clustering of the granules is largely prevented by cooling them during constant agitation in a

rotary cooler. Uncoated granules of this type will transmit light but the highly pigmented glaze effectively reduces this disadvantage. During the 1930s these granules raised the standards of the industry to a new level of color, durability, and freedom from staining.

Another coating that has attained outstanding commercial success was patented by Gundlach in 1931. This is formed by a low-temperature process in which phosphoric acid, zinc oxide, pigments, and other constituents are coated on dark-base granules, such as slate. This coating has advantages in processing expense and natural adhesion to asphalt and allows the use of very strong green pigments, such as chrome green.

As early as 1912, crushed pottery, brick and other ceramic materials were used, and they serve some needs today. Minor quantities are produced for specialties like white and crushed brick for siding.

Clays and shales were used by Atkinson in 1929 to produce colored brick-type granules. Colors can be developed from the pigments occurring naturally in the clay, added to the clay, or in surface coatings. This refractory material requires several hours of burning at temperatures up to 2220°F to reach the required hardness. Annual output of brick granules in recent years has averaged somewhat over 50,000 tons. Its best market is in the production of siding. Brick granules are produced in Pennsylvania, Indiana, and Illinois.

PROPERTIES, TESTS, AND SPECIFICATIONS

The following properties are characteristic of material that is to be used as a natural or base granule:

1. It should not disintegrate when exposed to the weather.
2. It should be tough enough to withstand handling through mechanical equipment without appreciable breakage.
3. It should be sufficiently uniform in physical and chemical composition to allow satisfactory processing control.
4. It should be opaque.
5. Various grain shapes, from equidimensional to very flat, have been used successfully, but consumers generally prefer the less extreme shapes because of their desirable embedding behavior.
6. The deposit must contain enough tonnage within economical haulage distance of the plant site to support years of production.
7. Low porosity is desirable.

Coloring Processes

Individual coloring processes have their own special demands. High-temperature glazes require a base rock that: (1) is nearly free of intrinsic color, (2) has a high silica content, (3) has a low content of impurities like clays and iron compounds, which interfere with processing, (4) has a very high melting point—approaching 3000°F.

Lower-temperature processes are less stringent in melting-point requirements, and if the coating is not too transparent dark rocks can be tolerated or even preferred, as they are opaque and also supply depth to the final color. Some formulas require special rock compositions and textures in order to develop a good color and coat. Moderate porosity is not objectionable for some purposes.

Producers of brick-type granules prefer white, buff, and red-burning clays and shales that will develop hardness as rapidly as possible. These will produce some salable products without additional formulation, and other colors can be developed on them by adding appropriate pigments and coatings.

Following is a list of materials that have been used on roofing:

- | | |
|---------------------------|---------------------------|
| 1. Silica sand | 12. Rhyolite |
| 2. Feldspar | 13. Various clay products |
| 3. Mica | 14. Shale |
| 4. Slate | 15. Basalt (trap rock) |
| 5. Greenstone | 16. Slag |
| 6. Siliceous river gravel | 17. Graywacke |
| 7. Quartzite | 18. Granite |
| 8. Quartz conglomerate | 19. Oyster shells |
| 9. Talc | 20. Mica schist |
| 10. Pyrophyllite | 21. Syenite |
| 11. Glass | 22. Clay |

Color of the finished product is of prime importance. Shingles are sold across the counter to people who choose principally on appearance. The shingle coated with the most attractive granules has a big sales advantage. That large quantities of natural and other granules of comparatively low color value find a good demand testifies to the fact that many people prefer conservative tones; in general, however, stronger, richer colors are in greater demand. Green is the most popular color, followed by red, black, and blue. In some products, notably buff, mottled colors are sometimes preferred, but generally solid colors are required.

Granules must be sufficiently durable to withstand the attacks of weather without excessive loss of color during the normal life span of the roofing. "Fading" may result from leaching or decrepitation of the bonding material, or from decomposition, or chemical reaction of the pigment itself. Attainment of the desired color and durability depends upon the selection of suitable pigments and adjustments in formula and processing conditions. Natural granules must also be tested for fading, as some rocks are colored by relatively unstable constituents.

Once a color has been established and standardized, only slight variation is allowable from shipment to shipment. To ensure consumer satisfaction, color variation should be so small that there will be little or no visible difference when shingles made at different times are applied side by side on a roof. On the other hand, it is not to the shingle

manufacturer's interest to set the limits unnecessarily close and increase costs of granule production to a point that makes the item unprofitable or higher priced.

Even under the most favorable conditions, the limits are uncomfortably narrow, because very small differences in tint are visible on a roof. Attractive mixtures of different colors have become so popular in recent years that the variegated shingle now predominates. These blends are prepared individually by each roofing manufacturer. Almost every inadvertent change in formula, base material, temperature, and other processing condition is reflected promptly in the color. Constant vigilance is required of production men to detect, diagnose, and correct or compensate for these variations as they appear. Accurate decisions are required because a kiln producing 10 to 40 tons per hour will rapidly accumulate carloads of off-color or otherwise unsalable stock.

Granules showing minor variations from standard can be mixed or "blended" with other granules that have a tint on the opposite side of standard. Intimately blended, they compensate for each other and match the standard color within commercial limits. Colors are made up of so many components that blending is something of a fine art. Thousands of dollars can be saved yearly by skillful blending. When granules show a major variation from standard, blending is useless because the mixture is then too mottled to resemble a solid-color standard. If such granules can be recoated and refired, at least their raw-granule value can be salvaged; if conditions make this impossible, they are discarded. High uniformity of quality can best be maintained by making sufficiently extensive runs to establish good control of processing conditions, eliminate contamination, and absorb blend that normally is produced in the early stages of a run.

In the production of natural and crushed-brick and pottery granules, color factors require selective quarrying or careful choice of crushing stock.

Fifteen years ago most granule manufacturers offered a comparatively simple line of colors, which included two or three popular items plus such other minor ones as were convenient, but more recently some producers have developed a great variety of specialties tailored to the desires of individual customers.

Durability

Granules and coatings must be hard and tough enough to stand the rough handling they receive in elevators, chutes, mixers, and long falls into bins. Lack of toughness shows up in broken granules, excessive build-up of fines, or badly abraded coating. Some protection can be given by lubricating the granule with oil or wax. This practice also serves temporarily to enhance the color and assist embedding.

The role played by porosity of granules in the problem of shingle blistering is a source of endless disagreement. The problem is complicated by the fact that shingle blisters are known to be caused by other factors also, such as moisture trapped in the felt and incompatibility of the saturating and coating asphalts. Laboratory tests devised by various groups indicate that moisture may pass through the capillaries of a porous granule or coating, and when heated in the sun this trapped water vaporizes and produces a blister in the softened asphalt. On the other hand, some extremely porous granules give satisfactory service, particularly on siding.

As one prime function of a granule is to protect the asphalt from the actinic rays of the sun, the granule should be opaque rather than transparent. A very transparent granule has the double disadvantage of poor adhesion to asphalt and loss of color owing to asphalt showing through it. Since the total opacity of a granule is the sum of that imparted by the base and the pigmented coating, a more transparent base requires more opaque coating.

Other factors also are important in the adhesion problem. Granules differ considerably in their natural compatibility to asphalt but special surface treatments have been developed that can largely overcome this disadvantage for the less favored ones.

Under some conditions, exceptionally high compatibility with asphaltic oils is not an unmixed blessing. Dark oils may creep from the asphalt around the granule, producing a "stained" shingle. Even transparent oil films may catch and retain particles of soot, particularly in the areas where bituminous coal is burned, and a "sooted" roof results. Fortunately, exposure of a freshly applied roof to the sun for a day or two generally will harden the oil film and remove the likelihood of sooting. This type of sooting should not be confused with the natural soiling that any roof gets in service, particularly in a smoky atmosphere.

"Bloom" is a term applied to a white layer of soluble salts deposited on shingles under certain conditions by the evaporation of solutions derived from the granule coating. It will wash off in the first rain and is of no importance if the solubility it indicates is not so high as to result in progressive loss of pigment and adhesion.

To give satisfactory service on a roof, neither the body nor the coating should rupture or disintegrate under extremes of weather. This necessitates careful selection of base and process and extensive testing under normal or accelerated weathering conditions.

Effect of Size and Shape

Grain shape is determined by the crushing characteristics of the material. Some consumers favor the flat fracture of slate because it covers the asphalt well. On the other hand, directional effect, which is

particularly characteristic of blue-black slate granules coated on the shingle, is disadvantageous. This feature is not as troublesome in other slates. Blockier granules can be embedded more easily into the asphalt, but spherical or equidimensional granules are not favored because asphalt often shows between them. A compromise between flat and equidimensional, something of a wedge shape, seems to describe the roofing manufacturer's preference.

Complete coverage is obtained by controlling the distribution of sizes in the grade, so that spaces between the large grains are filled by smaller particles. Special attention must be given to both the coarse and fine ends of the grade. Oversize grains may puncture the shingle and excessive fines will dust over the asphalt surface, interfering with adhesion of the larger granules. Exceptionally close attention must be given to grading because in the handling of large tonnages of granules through numerous pieces of equipment and processes the grade is subject to wide variation due to segregation, breakdown, and clustering.

Grading

Table 1 shows various grading specifications. These are typical but by no means universal—many variations are in use to meet special manufacturing problems in both the granule and roofing plants. All

TABLE 1—*Typical Grading Specifications for Roofing Granules*

Screen	No. 11 Grade						Typical No. 9 Grade		Typical No. 28 Grade	
	Blue-black Slate		Brick		Coated ^a					
	Mini- mum	Maxi- mum	Mini- mum	Maxi- mum	Mini- mum	Maxi- mum	Mini- mum	Maxi- mum	Mini- mum	Maxi- mum
Retained on:										
8 mesh....	0	0	0	0	0	0	5	15	0	0
10 mesh...	5	15	0	1	0	1	40	60	0	0
14 mesh...	25	45	15	25	25	35	25	40	0	0
20 mesh...	25	35	35	45	35	45	7	15	0	0
Minus 20-mesh							0	5		
Retained on:										
28 mesh...	10	18	25	40	20	30			5	15
35 mesh...	5	10	5	15	3	7			35	50
Minus 35-mesh	0	4	0	2½	0	2				
Retained on:										
48 mesh.....									25	40
60 mesh.....									5	20
100 mesh....									0	8
Minus 100-mesh									0	5

^a Artificially colored quartz, trap rock, greenstone, or slag.

but a small tonnage falls in the No. 11 classification. No. 9 and No. 28 represent the extremes of coarse and fine grades that normally enter the market.

Laboratory tests have been developed for the investigation and control of the various qualities. Some characteristics, such as disintegration, grain shape, and toughness, are largely established before the granule goes into production. Others can be strongly influenced by processing conditions, so intermittent tests must be run on production samples to maintain high quality. These may range from occasional checks on the less critical to very frequent (say every 15 min.) on important and highly variable qualities. Every organization has its own group of tests and instruments, and the following are mentioned only as examples. Various mechanical color analyzers have been tried for controlling color but none has proved as effective as the trained human eye. Adhesion tests range from determining the weight of granules rubbed from a shingle by a testing machine to tests that reveal the distribution of special treatments. Blistering can be measured by subjecting a granule-coated metal-backed asphalt panel to a carefully controlled cycle of heating and cooling, using vacuum to accelerate penetration of water. Solubility can be rated by boiling the granules for a definite period of time and titrating for some soluble compound. Grading is universally controlled through screen testing.

Bloom appears on some granules when water is added to a shallow dish of them and allowed to evaporate at low temperatures. Toughness is revealed by tumbling a sample back and forth in an iron pipe and determining the breakdown by screen analysis.

Although laboratory tests serve a very useful purpose, final evaluation of a new type of granule can be made only after several years of exposure under severe climatic conditions.

PREPARATION FOR MARKET

Ordinarily crude rock is produced in an open quarry and is loaded with a power shovel onto trucks or quarry cars for transportation to the plant. At one location, underground methods are used, and at another plant pebbles are dredged from a river bed.

The primary crushing usually is done with jaw and gyratory crushers in sizes commensurate with the desired capacity. Washing usually is unnecessary but deleterious fractions may be removed with wet systems of trommels or vibrating screens. Both vertical-kiln and rotary-kiln driers are used. The granules are made in gyratories, rolls, or hammer mills in closed circuit with a system of shaking screens and surge bins.

Natural granules may receive special surface treatments of oil or

waxes in tumbling drums, chutes, or screw conveyors and are ready for shipment at this point.

Waste fines, sometimes totaling 65 pct of the rock fed (but usually less than 50 pct), when not salable as a by-product, are moved by conveyors, draglines, trucks, railroad cars and cranes, or wet pumping systems to a waste pile or pond. Many plants have auxiliary equipment to further prepare their by-product fines to the customer's specification.

Crushing rock to granule size produces a great deal of dust, and as this dust is injurious to workmen, machinery, and near-by property, many plants have installed elaborate dust-collecting systems, usually of the blanket or electrical types.

Brick-type granules may be burned in a Herreshoff furnace or a rotary kiln to give them the required hardness.

It is desirable to have several hundred tons of storage-tank capacity for raw granules ready for coating, to avoid production delays.

In the coloring plant, properly sized raw granules are coated with the formula in a rotating mixer. Some formulas require drying at this point, and this may be accomplished by blowing hot gases into the mixer, passing the granules into or over a heater or preheating them before coating. The raw mix is fed into a rotary kiln or Herreshoff furnace, and as it travels to the discharge end the temperature rises to a point that will mature the coating. The granules discharge into a cooler, which may be a 40 by 6-ft water-cooled steel drum for high-temperature conditions or simpler air-cooled chutes. Temperatures are reduced to a level that will not damage handling equipment and final cooling takes place in storage.

A scalping screen set between the cooler and the loading station enables the operators to remove outsize material that may have built up in processing and ensures delivery of a proper grade to the customer.

Surface treatments of vegetable or mineral oils, waxes, resins, or other compounds may be applied in the cooler or later in special rotating drums, chutes, or screw conveyors.

A system of bins, rented or privately owned boxcars, and warehouses are used for blending and storing the finished granules before shipment. The smallest plants may have only a couple of bins whereas the largest plants need storage capacity of more than one hundred carloads.

Generally roofing granules are shipped in bulk in boxcars or hopper-bottom cars. They flow into the boxcar by gravity and may be distributed to both ends by shovel or wheelbarrow. A portable belt loader is used for this purpose at most plants. Provision must also be made for sacking at the loading station, as there is a considerable demand for sacked material by customers who have limited storage facilities.

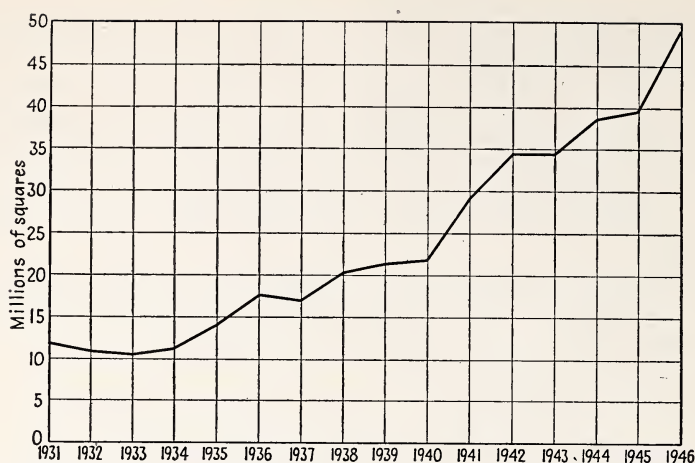


FIG 1—SHIPMENTS OF GRANULE-COATED ROOFING AND SIDING, UNITED STATES.
From U. S. Department of Commerce.



FIG 2—LOCATION OF PLANTS REPORTING PRODUCTION OF ROOFING GRANULES IN 1946
IN THE UNITED STATES.

MARKETS

Although small quantities of granules are sold for other uses, such as surfacing tennis courts, virtually the entire output of the industry is consumed in the manufacture of asphalt and asbestos roofing and siding.

Comprehensive statistics of granule production have been compiled only since 1942. As shown in Table 2, production was well maintained during the war and attained record levels after the end of hostilities. The demand for granules is sustained in periods of depression as well

as of boom because about 70 pct of the composition roofing output is absorbed in repair and maintenance. Although comparable figures of granule output are not available for the years prior to 1942, some conception of the rapid growth of the industry can be derived from Fig 1, showing production of granule-coated asphalt roofing.

TABLE 2—*Production of Roofing Granules in the United States, 1942-1947*

Year	Natural		Artificially Colored	
	Short Tons	Value	Short Tons	Value
1942	352,320	\$2,650,503	538,310	\$ 7,594,174
1943	287,090	2,190,143	543,870	7,745,452
1944	287,084	2,210,379	637,089	9,313,356
1945	355,840	2,628,052	628,220	9,124,891
1946	447,910	3,470,411	877,990	12,939,512
1947	504,980	4,166,810	1,133,870	17,905,899

Year	Brick		Total	
	Short Tons	Value	Short Tons	Value
1942	43,230	\$ 636,961	933,860	\$10,881,638
1943	47,650	716,685	878,610	10,652,280
1944	65,827	1,005,964	990,000	12,529,699
1945	61,220	947,637	1,045,280	12,700,580
1946	54,660	866,174	1,380,560	17,276,097
1947	56,570	998,434	1,695,420	23,071,143

Except for the modest tonnage that is shipped to Canada, virtually all the market for roofing granules is in the United States. More than one hundred plants are making composition roofing and siding in the United States. Most of them are east of the Mississippi but there is a substantial number along the West Coast. As shown in Fig 2, the granule plants are distributed similarly. Canada has 14 plants owned by 10 companies,³ which consumed 77,559 tons of granules in 1945, of which 62 pct was imported from the United States.

Prices

Prices of granules are comparatively low and, through the past years of rising labor and material costs, have increased very little. Most naturals bring \$6 to \$10 per ton at the plant and most artificially colored and brick granules \$12.50 to \$25. A few specialties range up to \$35 per ton.

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CHAPTER 19

GRAPHITE*

BY G. RICHARDS GWINN†

THE mineral graphite has been known for hundreds of years and was first used commercially as a coloring agent. Its true identity, however, was not recognized until the end of the eighteenth century and its commercial development did not become extensive until near the close of the nineteenth century. The common names for this mineral are graphite, plumbago, and black lead; others less frequently used are potelot, crayon noir, carbo mineralis, and kish. Graphite was named by Johann Gottlieb Werner in 1789 from the Greek word *graphein*, to write, and this name was applied primarily to the large crystalline, flake variety. Plumbago is a trade term used primarily for massive graphite as found in Ceylon. Black lead is also a trade term and, like plumbago, is based upon the idea that prevailed throughout the Middle Ages that graphite was a form of lead, or at least contained that metal.

Graphite is a soft, black, unctuous form of carbon that crystallizes in the hexagonal system with rhombohedral symmetry. It occurs occasionally in six-sided tabular crystals but usually is found in foliated masses, minute disseminated scales, or earthy lumps. It has perfect basal cleavage, is gray to black, has a metallic luster and a gray streak. The specific gravity is 2.1 and hardness is 1 to 2. It is opaque even in finest particles; extremely resistant to the action of acid or heat; and a good conductor of both heat and electricity.

Graphite may be separated into three classes: (1) natural, (2) manufactured (which is sometime called artificial), and (3) colloidal. Natural graphite is divided into two classes, "crystalline" and "amorphous." Crystalline graphite may occur as flake, lump, chip or dust. Amorphous graphite is a commercial term only, as all graphite is crystalline, but grades in which the individual grains cannot be distinguished are classified by the trade as amorphous. Natural mixtures of crystalline and amorphous occur in all proportions.

The term "artificial graphite" is a misnomer; "manufactured graphite" is a better term, because it actually is pure crystalline graphite,

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† Mineral Economist, Bureau of Mines, Washington, D. C.

the only artificial attribute being the method of production. Colloidal graphite is composed of manufactured graphite subdivided until the individual particles approach the dimensions of solids in true solution. These particles possess like electrical charges, which facilitate their suspension in liquids for long periods of time through the induction of repulsion fields that prevent intercollision, agglomeration, and settling.

The purest natural graphite contains almost 100 pct carbon, with very small amounts of silica. From this it may grade down to shales or slates containing only enough carbonaceous matter to make them black. Commercial graphite contains various impurities, the graphitic carbon content ranging from as low as 30 or 35 pct for the paint trade to 85 to 98 pct for crucibles, lubricants, batteries, and brushes. The proportion of impurities is commonly greatest in the flake deposits. The impurities usually are mica, calcite, quartz, feldspar, sulphides of iron (pyrite and pyrrhotite) and various silicates of lime, magnesia, and alumina.

Finished grades and classifications of natural graphite depend on the type of raw material and separation used. Several grades and classes of varying particle size and purity may be produced from one mine. Finished grades are classified under flake, crystalline lump, chip or dust, and amorphous. Flake is classified according to size of flake, carbon content, and percentage and kinds of impurities. Vein graphite is graded as needle lump, lump, chip, and dust. Needle lump, because of its fibrous structure, is a special-quality material and contains 90 to 95 pct carbon. Lump contains about 90 pct carbon; chip and dust contain, respectively, about 80 and 55 pct carbon. There is also a variety of Ceylon amorphous described as large lump (1 to 3 in.), which may contain 91 to 99 pct graphite carbon.

Amorphous graphite is often graded according to the locality from which it comes, as each deposit has its local peculiarities. Most amorphous graphite is the result of the metamorphism of coal seams, the carbon of which has been converted into the graphitic form. The purity of such graphites, therefore, depends on that of the original coal. The high-grade amorphous deposits of Sonora, Mexico, average 85 pct carbon. Amorphous graphite is also found finely disseminated in slates and shales. These graphitic slates, as a rule, are relatively low in carbon and some are too lean for refining. In such deposits, the acceptable material is hand-picked.

OCCURRENCE

Natural graphite is found in igneous, sedimentary, and metamorphic rocks. In igneous rocks, it has been found in iron-nickel meteorites, effusive and plutonic rocks, dikes and pegmatites. In sedimentary rocks, it has been noted as small detrital particles that have been transported and deposited along with other elastic minerals. Because of its soft-

ness, however, it may be ground to such small sizes that it is unrecognizable in these rocks. The commonest occurrence is in metamorphic rocks, schists, gneisses, and metamorphosed limestones. Rarely does it constitute more than 10 pct of the rock, although in a few deposits it comprises virtually the entire rock. In gneisses and schists, it is present in small, thin flakes seldom over $\frac{1}{8}$ in. in diameter, oriented parallel to the foliation and disseminated through the rocks like mica flakes in mica schists. The graphite flakes in limestone are similar in character but seldom show marked parallelism of orientation. In igneous rocks, including pegmatites, graphite also occurs in the form of unoriented thin flakes as well as pockets or lumps consisting almost entirely of graphite. In pegmatites, the flakes are normally much larger and considerably thicker. Graphite also occurs in the form of veins in which other minerals may be entirely lacking. Many veins show foliation but do not readily split into thin flakes or fibers. Finally, graphite occurs in bedded deposits recognized as former coal beds altered to graphite.

DISTRIBUTION OF DEPOSITS

Graphite is a widely distributed mineral found in virtually every country of the world. Most occurrences, however, have no economic importance because of poor quality, prohibitive mining and milling costs, inaccessibility, and poor location with reference to the industrial centers where graphite is used. The principal commercial deposits of graphite occur in Ceylon, Madagascar, Germany, USSR, the United States, Canada, Korea (Chosen), Mexico, Czechoslovakia, and Austria.

United States

The first domestic graphite mine was in Massachusetts—it was also one of the first mining ventures of any kind in America. It was first secured by a grant to John Winthrop, Jr. (son of Governor Winthrop, of Massachusetts), who purchased the tract from the Indian inhabitants between 1644 and 1658. The preliminary operation appears to have been unsuccessful but in 1738 mining was resumed and one or more shipments were made to England, where the material brought 4 pence a pound.¹³ Flake graphite deposits in schists or gneisses have been mined in New York, Pennsylvania, Alabama, Texas, and California, and amorphous graphite has been mined in Michigan, Georgia, Rhode Island, New Mexico, and Nevada.

Deposits of vein graphite near Dillon, Montana, occur near the southwest end of the Ruby Range of mountains, 15 miles southeast of Dillon, at an altitude of 7500 to 8000 ft. They are found in seams in limestone, as pockets in marble, and in schists associated with garnet, mica, quartz, and feldspar. The seams in limestone are 1 to 2 in. wide and persist over a considerable distance parallel to the bedding of the

rock. Graphite in the marble occurs in irregular bunches and pockets at the contact of the marble and the igneous intrusion. In the schists, it is intimately associated with garnet, quartz, feldspar, and mica. Production from these deposits has always been small.

Deposits of flake graphite, from which the largest amount of graphite has been recovered, are found in schists and gneisses that show various stages of weathering, ranging from the slightly altered schists containing the hard siliceous ores of the eastern and southern Adirondacks to the weathered claylike masses typical of some of the Alabama deposits.

Deposits in the eastern and southern Adirondacks of New York state can furnish a large amount of flake if necessary, but the graphite is in hard rock and is interleaved with biotite mica, which makes separation difficult. The rock contains 4 to 5 pct graphite and therefore is of higher grade than that occurring in Alabama. A small area near Suffern, New York, yields graphite in large flakes, but here, again, it is in narrow veins in fresh, unweathered gneiss and would necessitate mining and treating a large tonnage of rock to obtain a small amount of graphite. The graphite on the western edge of the Adirondacks near Morristown is foundry-grade material and the tonnage is small.

Graphite has been mined intermittently in Pennsylvania for some time. The principal producing deposits are about 30 miles west of Philadelphia, in the gneiss of Pickering Valley, Chester County, and blocked-out reserves of 4 to 5 pct contain a large tonnage of flake material.

Deposits of moderate-size flake have been mined for a number of years in Alabama. Up to 1930, the production was 1,500,000 tons of material containing 2 pct graphitic carbon, 45 pct of which was plus 65-mesh. Flake deposits are best developed in a comparatively narrow belt approximately 4 miles wide and 60 miles long, extending in a general northeast-southwest direction through portions of Clay, Coosa, and Chilton Counties. The graphite occurs in weathered schist and is recovered by open-pit mining. During World War II, 5409 short tons of flake graphite was produced in this region.

The Texas graphite deposits are found in the central region between Llano and Burnet, in a fresh siliceous schist. Both flake and amorphous varieties are found, and the material is chiefly of foundry-facing grade. A small tonnage of large flake could be recovered but under present manufacturing processes the flake is too soft for use in crucibles.

Graphite in California occurs in Calaveras, Mendocino, Los Angeles, and San Diego Counties as flakes disseminated through a schist, which takes the form of a vein of schist in granite. The graphite is crystalline but in small flakes associated with quartz, feldspar, and minor amounts of mica and pyrite.

Graphitic slate classed as amorphous graphite has been produced in considerable quantities near L'Anse, Barago County, Michigan, and in the vicinity of Cartersville, Georgia. In Rhode Island, amorphous-graphite beds were formed as a metamorphic product of coal beds. The coal beds originally were of moderate thickness but were folded and compressed by movements in the crust of the earth. Pressure was so intense that the coal was squeezed into pockets, which are joined by thin stringers consisting of coal, quartz, feldspar, pyrite, and other impurities. The heat generated by the movement and compression has driven off many of the volatile constituents of the coal, leaving impure amorphous graphite as a residue.

Amorphous graphite has been formed by the alteration of coal in New Mexico. In Colfax County, along the Canadian River 7 miles southwest of Raton, igneous intrusions have altered bituminous coal to coke, and in a few places where the heat was particularly intense graphite was formed. Near Carson City, Ormsby County, Nevada, a graphitic shale has been mined intermittently for amorphous graphite for some time.

World Deposits

Although graphite is found in virtually all countries of the world, Ceylon, Madagascar, and Korea stand in the forefront because of the high quality of the graphite produced there, the cheapness of native labor, and favorable mining conditions. Certain other localities have attained prominence because of low production cost and ease of transportation to the consuming markets. The large output of Czechoslovakia, for example, is the result as well as the cause of a great local industry utilizing its products. Among the localities that are minor or potential producers are small deposits in England and Scotland; Berttula, Finland;¹⁴ Vittangi and Norberg, Sweden; Senjen, Norway; the Machokos district in Kenya (East Africa); the Victoria and Wankie districts (Rhodesia); Uganda; British South Africa; Belgian Congo; the Bambari district of French Equatorial Africa; Portuguese East Africa; the Departments of Suceara, Gorji, and Nehedenti, and the Carpathian Mountains, Rumania; Mt. Bopple, Queensland; Munghlinup and Kenenup, Western Australia; Eyre's Peninsula, South Australia; Undercliffe, New South Wales; Chile, Paraguay, and Uruguay in South America; Shansi, Chihli, Kiangsu, and Hunan in China.

NORTH AMERICA

Canada—Graphite is widely distributed through Canada but the only deposits that have been worked extensively are in southern Quebec and Ontario. The commercial deposits occur in gneiss, crystalline limestone, and contact-metamorphic zones. For many years

more than half the total Canadian output was furnished by the Black Donald mine, at Calabogie, Renfrew County, Ontario. The occurrence consists of small flake containing local streaks of larger flake. The graphitic carbon content ranges from 60 to 80 pct. The graphitic material enclosed in limestone is of metasomatic origin and constitutes a replacement product of a certain zone of the limestone enclosing the deposit. The alteration of the limestone apparently involved intense graphitization accompanied by a corresponding lesser degree of silicification.²⁶

Newfoundland—A considerable quantity of amorphous graphite has been produced near St. John's, Newfoundland, and a few tons of vein graphite have been mined from Baffin Island, Labrador.

Mexico—Deposits of amorphous graphite are found in the states of Sonora, Oaxaca, Guerrero, Hidalgo, Coahuila, and Baja California. The bulk of the production comes from mines in the state of Sonora, about 20 miles south of La Colorado. The Oaxaca deposits are said to be too high in impurities to be commercially profitable.

The Sonora graphite was discovered in 1867 but commercial operations did not begin until 1895, when the U. S. Graphite Co., the present owner, purchased and developed the property. These deposits originally were coal seams enclosed in sandstone. The coal was altered to graphite by the heat that attended intrusion of granite into the sediments. There are at least six beds, two or three of which are of good quality and commercial size. The largest averages 9 to 10 ft in thickness, but, being highly folded, its thickness reaches a maximum of 24 ft. The graphite is exceptionally pure, selected samples containing as much as 95 pct graphitic carbon, the average being 80 and 85 pct.

EUROPE

Austria—Austria has greater resources of graphite than any country in the world and before its dismemberment annually produced more than one third of the world's output. The greater part of Austrian graphite is amorphous or so finely crystalline that it is classified as low-grade material. Production is derived from deposits in four distinct fields—the Krumau and Schwarzbach districts of Bohemia, Moravia, Lower Austria, and Styria. The first two are in what is now known as Czechoslovakia and will be described under that country. Flake graphite occurs sparsely disseminated in gneiss in Lower Austria in an area along the left bank of the Danube, between 39 and 55 miles west of Vienna. Amorphous graphite is found in graphitic slates situated between gneiss and mica schist, and in the Muehldorf district a steeply dipping bed of impure graphite occurs in crystalline limestone. The graphite produced in Lower Austria, even after refining, contains only 60 pct of carbon and is employed chiefly in foundry facings. The

graphite in the Styrian Alps is found in highly folded slates and limestones and is derived from the metamorphism of coal seams. The crude material runs 40 to 95 pct carbon and needs only hand sorting.

Czechoslovakia—There are two graphite fields in Czechoslovakia, one in Bohemia and the other in Moravia. The deposits are irregular lenses of graphite schist interbedded with other metamorphic rocks. The major production from both fields is amorphous graphite, although a little crystalline material is mined in Bohemia. The refined product contains about 60 pct carbon and is used chiefly in the manufacture of foundry facings and cheap pencils.

Germany—The graphite deposits of the Passau district, Bavaria, are well known. The graphite occurs in lenses and pockets in gneiss and schists and is of the disseminated flake type. The gneiss is deeply weathered in many places, and the graphite is therefore easy and cheap to mine. The average graphite content ranges from 20 to 30 pct. During the Middle Ages, some of the alchemists' crucibles are said to have been made from this material.

ASIA

Ceylon—Deposits of graphite in Ceylon were reported in 1681 but commercial production began in 1827 and has been continuous since 1834. Graphite is widely disseminated through the rocks but, except for a few flake deposits, all known commercial occurrences exist as veins formed by the filling of fissures in gneisses and schists. Graphite workings cover nearly the entire southern half of the island. In the smaller veins and in a narrow zone between the main portion of many of the large veins and the country rock, graphite occurs as a mass of parallel fibers or needles normal to the vein walls. This fibrous material, known as needle lump, commands a premium price. Graphite in the larger veins has a coarse, platy or foliated structure.

Although the veins usually consist entirely of graphite, some of them carry other minerals in appreciable amount. Pyrite and quartz commonly occur in disseminated form or as bands and other accessory minerals are biotite, orthoclase feldspar, apatite, allanite, rutile, and pyroxene (usually augite). In some of the veins, the material has been crushed by later tectonic disturbances.

The veins are worked either by opencut methods or by vertical shafts. Except for three or four properties, which however, are the major producers, the mines consist of shallow pits or gougings in vein outcrops, which are leased to natives by the owners and are worked by hand methods.

Korea—The graphite industry in Korea dates from about 1903, when the first exports were made. Most of the graphite is amorphous, although some crystalline graphite is produced in the northern part

of the country. The amorphous graphite occurs as irregular and disconnected bands and lenses in schists, shales and phyllites formed by the alteration of coal beds. Some of the amorphous graphite deposits in the Kyeing-Sand district are of great width, reaching 18, 47, and 78 ft, respectively. Recent investigations have shown that some of the schists and gneisses are of Permian age, rather than pre-Cambrian as previously reported by the Japanese. The crystalline graphite in northern Korea is reported to be vein material comparable to the coarsely crystalline lump and chip graphite of Ceylon.

USSR—Since the greater part of the graphite of the Soviet Republic is in Siberia, all of the occurrences are described under Asiatic deposits. The graphite deposits in the republic are of two principal types: (1) amorphous graphite containing small amounts of pyrite, formed by the alteration of sediments by the intrusion of igneous rocks, and (2) of regional metamorphic origin, consisting of flake graphite in crystalline schists. Until recently, the only graphite deposit in European Russia on which information was available was the Dzimorsk district, in the Caucasus. Here amorphous graphite occurs in large beds or lenses with an average thickness of 1 meter and a known extension of 1500 meters. As a result of geological exploration in the past 10 years, 37 graphite deposits of the contact-metamorphic type have been found in the Ural Mountains. The largest deposits of this type are found in eastern Siberia, at the Kureishoe, Noginokoc, Botogolskac, and Sretenskoe mines. Large deposits of flake graphite are found at Soyuznoc (Malo-Khinganski), near the Amur River.

AFRICA

Madagascar—The island of Madagascar probably contains the largest reserves of crystalline graphite of any section of the world. Graphite occurs in a belt of schists and gneisses almost 400 miles long. Most of it consists of flake but minor amounts of vein and amorphous material have also been found. The flakes are unusually large and constitute a much greater percentage of the schist than in any other large known deposits. Weathering has altered the rocks to a mixture of clay, graphite, mica, and quartz, which makes mining comparatively simple. The graphite content averages 10 to 12 pct but may be as high as 40 to 60 pct.

POLITICAL AND COMMERCIAL CONTROL

Graphite is one of the so-called minor nonmetals that attain major importance during war periods. World requirements in terms of tonnage are relatively small, and uses have changed so greatly in the past 25 years that different types, with few exceptions, are more nearly interchangeable in use. However, the quality of the flake graphite re-

quired for crucibles and amorphous graphite for some graphite brushes and batteries is exacting and, under current mining and manufacturing practices, only a small part of the world production can be utilized economically by these industries. Graphite for crucibles is supplied largely by Madagascar; graphite for brushes utilized in electric motors in high-altitude aircraft equipment, and some batteries, is obtained entirely from Ceylon. Quantitywise, however, Mexico and Korea supply perhaps the largest percentage of the graphite consumed by industry.

Political and commercial control of the graphite industry in times of war is becoming less important. Germany and Austria proved their independence of Ceylon graphite in World War I and of Madagascar graphite in World War II. The quantities of crucible-grade flake required by the United States have also declined steadily during the past 20 years. However, Great Britain and France, through their possession of Ceylon and Madagascar, still possess a commercial and strategic advantage.

Although the United States has large supplies of graphite and manufactures great quantities of graphite products, the domestic graphite industry prospers only during war times. During World War I, Ceylon graphite was the standard product for the manufacture of graphite crucibles. The lack of shipping and embargoes by the British, to prevent this material from falling into the hands of the enemy, cut off our supply, and about 35 mines and mills began operation in Alabama. At the end of the war there were many failures in the domestic industry because of the large stock piles of graphite available in many parts of the world and the poor classification and grading of domestic material. Again, during World War II, because of the fall of France to Germany in 1941, the Japanese expansion southward, which threatened our supply of Ceylon graphite, and the shortage of shipping, the domestic industry was revived to supplement imports and to act as insurance in the event of the complete stoppage of imports. Extensive field and laboratory investigations were made by various federal agencies before mills were erected or Government loans made to existing plants. Thus only a few additional plants were put into operation. By the end of 1943, the import situation improved, and it was no longer necessary to continue Government assistance to mine and stock-pile the relatively high-cost domestic material.

Tariffs have been levied and trade agreements between the United States, the United Kingdom of Great Britain, France, and Mexico have been drawn up, but they have had little effect on the market for domestic graphite except during war time.

The domestic graphite industry has been handicapped by other factors as well as high costs. Among them are: the presence of large but low-grade deposits of irregularly shaped and relatively soft flakes,

lack of knowledge of operating costs, and in some cases, an almost complete ignorance of the size and shape of the deposits. Mills have been built on the basis of the analysis of a sample, which might not be taken as an average for the deposit. Too little attention has been paid to the associated minerals and the ease or difficulty of separation of the graphite from the gangue. This has been reflected in the production of a low-grade, nonuniform product. The graphite-consuming industry thus has become prejudiced against the domestic product and favors the more uniform imported material. Domestic producers, however, are now making strong efforts toward producing a more uniform product.

PRODUCTION AND CONSUMPTION

A summary of domestic production and consumption of all types of natural graphite in the period from 1930 to 1947 is shown in Table 1. The relatively low production figures for 1930 to 1934 reflect the industrial depression during that time. Revival of the domestic industry during World War II accounts for the increased production reported for the period from 1940 to 1944. The marked similarity of the totals for imports and consumption during the entire period indicate the dependence of the domestic graphite-consuming industry on imported material. Exports of graphite by the United States have always been small.

TABLE 1—*Production, Imports, Exports, and Consumption of Graphite in the United States*
SHORT TONS

Year	Production	Consumption	Imports	Exports
Five-year averages:				
1930-1934.....	558	10,441	11,001	1,119
1935-1939.....	642	23,780	23,873	1,161
1940-1944.....	4,972	37,392	34,211	2,603
1945.....	4,888	39,866	36,286 ^a	1,308
1946.....	5,575	36,402	33,140 ^b	2,313
1947.....	4,387	17,353	43,659 ^c	1,546

^a Includes 154 short tons of manufactured graphite.

^b Includes 4 short tons of manufactured graphite.

^c Includes 28 short tons of manufactured graphite.

What is believed to be a reasonable estimate of world production of graphite for the period from 1930 to 1947 is shown graphically in Fig 1. Output by the major producing countries, with the exception of the USSR, is also shown. As reliable figures for the production of graphite in the USSR are not available for much of the period, totals for that country are not included. The world-wide depression of 1929 and the early '30s is reflected in the decline in world output, which reached a low in 1932. Production expanded greatly in all countries

during the recent war period, reaching a peak in 1942 or 1943. Korea (Chosen) shows perhaps the largest gains and also the largest period of expansion. This is attributed to the demands of the Japanese war machine. The decline in 1945 and 1946 reflects cessation of hostilities and the period of readjustment necessary after a long war.

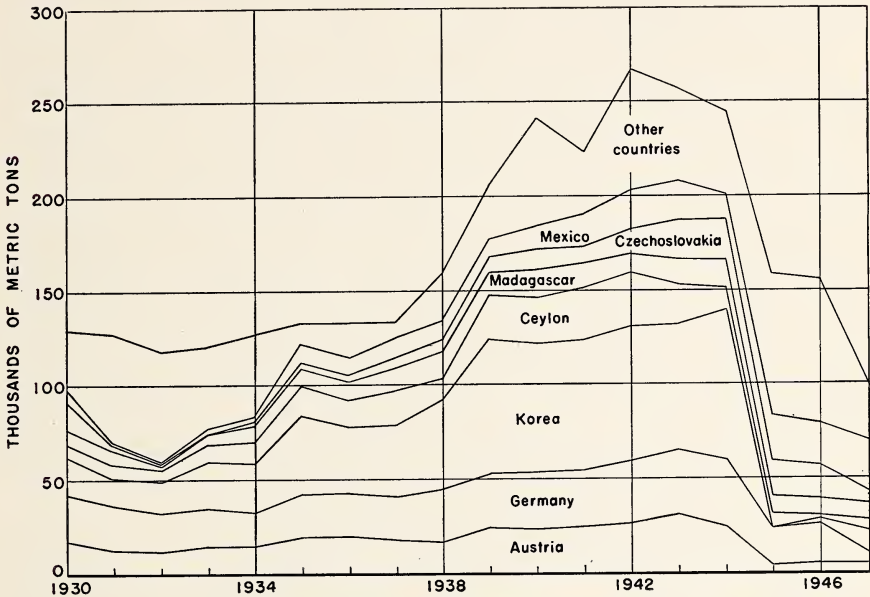


FIG 1—WORLD PRODUCTION OF GRAPHITE.

The United States, England, Germany, France, Japan, and Russia, the major industrial nations of the world, are the principal consumers of graphite. The use of graphite crucibles in the manufacture of steel and other metals, which started about 115 years ago, marked the beginning of large-scale consumption of graphite. Until about 1920, the manufacturers of crucibles, stoppers, nozzles, stirrers, and phosphorizers utilized about 75 pct of the world's output of graphite. However, with abandonment of crucible melting by many foundries and steel mills in favor of electric furnaces or other processes, together with improvement in the manufacture of crucibles, which now stand 60 to 80 heats, considerably less high-grade flake is necessary for industry. Annual consumption of crucible-grade graphite in the United States alone dropped from about 20,000 short tons in 1912 to about 5000 tons in 1944, a war year. Consumption in 1946 reached 3000 to 3500 tons. Pencils, lubricants, and other graphite products, which utilize, for the most part, amorphous material, are now the major consumers of graphite.

PROSPECTING AND EXPLORATION

The black color and unctuous feel of graphite make it easily recognizable, even by the layman. Perhaps this fact is partly responsible for the many failures in the domestic graphite industry. A large number of mines have been opened and mills built with little more prospecting than a preliminary survey of the surface outcrop, shallow trenching, or the chemical analysis of a sample.

Flake graphite commonly occurs in schists and gneisses, rocks that have been extensively altered, squeezed, and folded. Graphite deposits occur in streaks or lenslike bodies that merge more or less gradually into leaner material that may or may not be economical. The depth of weathering is also an important consideration in domestic as well as foreign deposits. As graphite is a relatively low-priced product, the costs of milling hard rock are prohibitive, and with present mining and milling practices only the weathered part of the deposit can be mined economically. In addition to the size or extent of the deposit, the nature of the material and the associated minerals must be determined. The percentage of graphite that can be recovered is as important or more important than the percentage of total graphite present in the deposit. The size and toughness of the flake, the quantities of mica, pyrite, and other undesirable impurities present, and the cost of separation of the graphite from these impurities must also be determined.

It is imperative, therefore, that a thorough program of prospecting and exploration be carried out to determine whether a given deposit is of commercial size or quality. This program should include an outline map of the outcrop of the deposit, surface trenching, and systematic drilling. Diamond drilling is perhaps the most reliable method of proving the deposit. A churn drill may be used, but to get accurate results the casing must always be kept near the bottom of the hole, to prevent material abraded from the upper bed from being washed down into the cuttings. This washing would give an exaggerated picture of the actual thickness of the deposit. As a supplement to the churn drill, a few test pits might be sunk to check the drill-hole records.

MINING METHODS

Most domestic graphite mines are small, shallow pits and do not present any unusual mining methods. Overburden is stripped off by scrapers or bulldozers and the weathered graphite-bearing rock is moved by power shovels and trucks. In some places, occasional blasting with a small charge of powder is necessary to loosen the material. Large-scale mining of Ceylon vein graphite involves considerable expense, because the veins dip steeply, which necessitates underground operating equipment. Bedded deposits of amorphous graphite in Mexico

and Korea are typical deposits of high-grade graphite of this type. As the beds are folded and pinch and swell on the limbs of the folds, graphite mining in these countries is carried on in underground workings.

PREPARATION FOR MARKET

Flake graphite, because of the nature of its occurrence, must be subjected to a cleaning process to separate it from the associated gangue. The character of the graphite in the particular deposit and its intended use determine the extent of the cleaning and refining process.

Domestic flake graphite is usually beneficiated in three stages: (1) preliminary or coarse grinding in a jaw or gyratory crusher, which separates the larger impurities, (2) refining this concentrate by further grinding in a ball or rod mill, and (3) final concentration by flotation. The product from the primary crusher may go to a storage bin or directly to the ball mill. The second step may be wet or dry grinding. The product from the ball mill is passed through a vibrating screen to the rougher cells of the flotation unit; the oversize from the screen is returned to the ball mill. A flotation process is believed to be the most efficient means of obtaining a clean concentrate and, at the same time, the maximum amount of large flake, because mechanical sifting will not eliminate all the impurities unless grinding continues to the point where the size of the flakes is greatly reduced. Successful flotation can be achieved with a number of reagents and under a wide range of conditions. The use of a frother alone is usually sufficient to obtain satisfactory separation of fine flakes but coarse flakes require a small amount of an oily collector to ensure their recovery. Depression of the gangue minerals is often more difficult than flotation of the graphite, and acid and alkaline reagents have been used to separate the gangue from the concentrate.⁸ The flotation concentrate is filtered and then dried. During or after the drying, dust is removed by air separation, and in some mills a 200-mesh air-floated product is obtained during the cleaning process. The dried product is screened, passed over an air table to obtain a uniform product, and bagged for shipment.

Physical methods for the separation and beneficiation of flake graphite furnish at best a product containing about 90 to 94 pct carbon. Chemical methods can be used to remove the remaining amounts of silica and silicates but costs at the present market price for graphite are prohibitive.

Processing vein graphite in Ceylon is comparatively simple and consists of preliminary hand sorting at the mine and later grading by combined manual and machine methods. The first process consists of breaking the large lumps of graphite by hand as they come from the mines. This eliminates the major portion of the impurities, which are quartz, orthoclase feldspar, pyrite, and other wall-rock minerals. The

lumps are broken again and the fragments are rubbed and polished by hand on a piece of wet burlap. The smaller material goes to a sifting machine, which separates it into small lumps, chips, and dust. The most successful processing of Mexican graphite is by grinding and air separation. Among several methods of air separation is one in which the ground material is fed onto cloth bolting stretched over agitating tables whose tops are perforated with a series of holes or jets, through which compressed air is forced. The graphite, which is light, moves off the end of the table, whereas the heavier gangue spills off the side. Another type consists of a vertical stream of air under pressure, which lifts the ground material upward. The gangue, being heavier, falls to the floor, whereas the graphite strikes a curved roof surface and is deposited on an adjacent table.

Amorphous graphite also occurs disseminated in slates, in which it makes up only a small portion of the rock. This material is ground without separation and is sold to the paint trade for use in pigments.

TESTS AND SPECIFICATIONS

Uniform tests for the particular grades of graphite required for specific uses are not available. The domestic graphite-producing, importing, and consuming industries are relatively small and individual members of each branch have their own tests, many of which are guarded as trade secrets. However, certain general statements can be made concerning the specifications or suitability of graphite for various uses.

Crucible-grade flake graphite ranges in size from 20 to 50-mesh, and should contain 83 to 90 pct graphitic carbon. Flakes larger than 20-mesh decrease the density of the crucible, detracting from its strength, and flakes smaller than 50-mesh do not have enough covering power to make a satisfactory crucible. Most manufacturers are agreed, however, that there is nothing to be gained by using a graphite containing more than 85 pct carbon because the higher carbon content contributes to reduced toughness of the flake. They also feel that the uniformity of the carbon content of the graphite from shipment to shipment is almost as important as the actual carbon content. Tough flakes of regular pattern are also required. Such flakes suffer less from breakdown during mixing. Madagascar flake is favored for this use because of its toughness and shape, which approximates parallelograms or polygons. Breakdown is confined primarily to reducing the thickness of the flake without altering the shape. The burning rate of graphite utilized for crucibles is considered of secondary importance, because crucibles usually fail from abuse long before the graphite is burned out. In the lubricating and pencil grades of graphite, the carbon content, which ranges from 95 to 97 pct, the abrasiveness of the ash, the silica, and

free sulphur content are important considerations. Finally, graphite for use in brushes on aircraft equipment, which operate in high altitudes, must contain 97 to 98 pct graphitic carbon.

MARKETING AND USES

The value of graphite to industry is based upon suitable application of one or more of its inherent qualities, such as unctuousness (which often is incorrectly referred to as greasiness); refractoriness, or ability to withstand high temperatures; conductivity of heat and electricity; inertness to a large range of reagents; and miscibility with other materials and with liquids. It is used in the manufacture of graphite crucibles, stove polish, lubricants, paints, lead pencils, foundry facings, dynamo brushes, electrodes, dry batteries, fertilizers, and many less important articles. Although graphite is subjected to concentration and refining at the mine, several additional operations are required in its marketing. Most crucible manufacturers purchase a prepared or blended product produced by companies engaged solely in importing and blending graphite to meet certain specifications. Some foundries purchase graphite from the mine and grind it to their own specification for foundry facings; others purchase the foundry facings from custom grinders.

Crucibles—The fair thermal conductance and high melting point of graphite are the characteristics that qualify it for a number of refractory uses—the manufacture of crucibles, crucible covers, pouring nozzles, crucible rests and stools, funnel or extension tops, skimmers, phosphorizers, ladle stoppers and stopper sleeves, pyrometer sleeves, furnace bricks and doors, annealing boxes, and case-hardening containers. For this purpose, Madagascar flake has been specified as essential. When mixed with clay and sand, and later fired, graphite imparts a resistance to sudden heat changes and a degree of heat conduction unequaled by most metals.

Pencils—The use of graphite as a pencil or in the manufacture of pencils is one of the earliest and by far the best known use of this material. In the sixteenth century, crayons were made in England from graphite obtained in the Borrowdale mine, in Cumberland. Solid blocks of the natural material were cut into sticks and sold as such. Later, they were cut somewhat smaller and protected by a wooden holder. The present method of making pencil "leads" from a manufactured mixture of graphite and clay was started near the close of the eighteenth century. The clay serves as a binder or plasticizer, to facilitate molding of the graphite and as a means of regulating the hardness and uniform quality of the "lead."

Although the name "lead pencil" is misleading, finely divided metallic lead is sometimes added, together with carbon black or anti-

mony oxide. Although hardness can be regulated by the proportion of clay, it is influenced also by the method of preparation, compression, and other factors.

The Borrowdale mine was exhausted and closed in 1833. Some 15 years later a similar graphite was found in the Sayan Mountains, west of Irkutsk in Siberia. This became the well-known Alibert mine, which supplied the Faber pencil factory in Nuremburg, Germany, for many years. After this mine was exhausted or abandoned, pencil manufacturers began using different types of graphite. Bohemian grades, which have a reputation for blackness, have been used largely, but at present the Mexican amorphous material is in great favor because it can be used without much if any admixture of other graphites.

Lubricants—Graphite is valuable as a lubricant because it adheres readily to metal surfaces and fills the pores, thus giving a veneer that reduces the bearing coefficient of friction virtually to that of graphite itself. The veneer is also protective, being resistant to most chemical and corrosive reactions. Flake graphite is preferable, as it readily forms a scaly layer on the metal, which is essential for successful solid lubrication, whereas extremely fine graphite tends to flow excessively with the oil supplied to the bearing. Graphite is used also for dry lubrication where oil or grease might be detrimental and where liquids of all sorts are to be avoided, as, for instance, on the bridges of pianos, organs, and textile machines.

Foundry Facings—Small flake of comparatively low carbon content and amorphous graphite are used for foundry facings. Except for the universal requirement of extreme fineness, the preparation of facings follows no generally accepted standard; therefore, probably there are as many formulas as there are manufacturers. The usual practice is to mix the graphite with sand, clay, talc, or mica. These impurities are present in many low-grade graphites, therefore very little refining is necessary in the preparation of this commodity.

Paints—Any impure natural graphite may be used in the manufacture of paints. Pure graphite is unsuitable, as it tends to coagulate in the oil vehicle and spread under the brush into an excessively thin coating. Impure graphite containing substantial quantities of silica can be mixed with iron oxide or zinc compounds to make a satisfactory pigment for paints employed for the protection of bridges, railroad cars, smokestacks, boiler fronts, tanks, and metal roofs.

Brushes—In most electric motors and generators, current is conducted from an outside source to the revolving parts of the motor by a number of small brushes. Because of its electrical and mechanical properties, carbon, in the form of natural graphite, manufactured graphite, or a combination of the two, is the most efficient material for the manufacture of these brushes. Carbon graphite brushes consist of finely

ground petroleum coke and varying quantities of natural graphite. Graphite brushes use the natural material almost entirely, and brushes used in aircraft equipment, which operate at high altitudes, use only Ceylon amorphous graphite containing 97 to 98 pct graphitic carbon.

Miscellaneous—Amorphous graphite is used as a conducting coating for electrotyping forms. For stove and shoe polishes, it is worked into a paste with clay, resin, and soap, an oil or water vehicle being added if a liquid variety is required. Carbon black may be added to intensify the color. Flake graphite is used in compounds employed to prevent scale in boilers. The small flakes gradually penetrate cracks in the scale and intrude between it and the metal, thus making it removable. The amorphous variety or fines from vein or flake graphite may be used to polish shot or to render gunpowder grains waterproof. They are also used as a filler in fertilizers, to give the required dark color and to coat the particles, thus preventing absorption of moisture. Similarly, they are used to coat tea leaves and coffee beans to protect them from moisture and to improve their color and general appearance. Flake, vein, or amorphous graphite is used as a dry-battery filler. As pure material is required, manufactured graphite is often preferred. Grain size is not important, and of the natural graphites, Mexican amorphous is favored by the trade.

PRICE HISTORY

Because of the many varieties and grades of graphite and the variation in supply and demand for particular grades, it is difficult to determine the market price for graphite. Many sales are based on negotiations between individual buyers and sellers. The majority of graphite buyers in the United States have long been accustomed to standard foreign material and are reluctant to experiment with domestic grades.

Prices are quoted on lump, chip, dust, flake, and amorphous graphite. The first three-named products are from Ceylon; flake includes Madagascar, Canadian and domestic materials; amorphous includes Ceylon, Mexico, Korea (Chosen), and domestic. All classes except amorphous, which is quoted by the ton, are reported in cents per pound. All prices are nominal, and for imported graphite are based, as a rule, on delivery in New York, landed and duty paid.

Ceylon carbon-lump graphite brought 2 to 3¢ per pound in 1937, increased to 9 to 10¢ in 1942 and remained at that level in 1947. Crystalline lump from Ceylon increased from 5¢ per pound in 1930 to 10 to 12¢ in 1943, where it has remained. Prices for chip and dust have been, respectively, 70 to 75 and 40 to 50 pct of those for lump. Although ocean freight rates increased during World War II, the reduction in the value of the British pound kept the prices of Ceylon graphite at a relatively low figure compared with the 32¢ per pound reported

in 1917. Prices for Madagascar flake were 2 to 3¢ per pound in the early 1930s and remained essentially unchanged until 1941, when the increase in ocean freight rates from \$14 to \$40 per ton raised the price of flake to 8 to 10¢ per pound. Prices in 1947 were 9 to 16¢ per pound. Crude amorphous graphite sold for \$10 to \$20 per ton in 1935 and in 1947 prices ranged from \$16 to \$32 per ton. Average prices for domestic flake graphite in 1930 were 4 to 6¢ per pound. Premium payments for this flake during the 1942–1945 period increased prices to 5 to 14¢ per pound. In 1947, average prices were essentially the same as the prewar period, ranging from 3 to 7¢ per pound.

MANUFACTURED GRAPHITE

A method for producing manufactured graphite was patented by Gerard and Street in 1893. The commercial method, an adaptation of the carborundum process, was patented in 1896, and production started in 1897, when 162,000 lb of graphite electrodes were made by the direct conversion of rods made from a mixture of petroleum coke with tar as a binder into graphite. The first plant was built at Niagara Falls, New York. The original discovery that graphite could be produced in the electric furnace was made in the course of experimenting with the effect of high temperatures on carborundum. It was found that carborundum is decomposed at about 7500°F, the silicon being vaporized and the carbon left behind.¹⁸ A process was later developed for making graphite from anthracite culm or petroleum coke with smaller amounts of quartz, sand, and sawdust. The material is crushed fine and placed in a long, troughlike furnace having an electrode at each end. On heating, carbides of the various metallic constituents of the ash are formed first; when the temperature is raised further, they decompose, leaving graphite. A purity of 99 pct graphite is guaranteed. There are now several plants in the United States, Canada, and other countries of the world.

Manufactured graphite competes with natural graphite in many uses; among them: self-lubricating bearings, mold wash in steel mills, pencils, crayons, paints, polishes, and powder glazing. Perhaps the most dramatic and widely publicized application of this material was announced in August 1945, when it was revealed that manufactured graphite was used as a moderator in the plutonium piles in the atomic energy plants at the University of Chicago and Hanford, Washington. About 10 to 12 grades of manufactured graphite are marketed, and prices range from about \$30 to \$300 per ton.

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CHAPTER 20

GYPSUM*

BY T. R. LIPPARD†

PURE gypsum may be broken down into its constituents as follows:

$$\text{Gypsum (CaSO}_4\cdot 2\text{H}_2\text{O)} = \left\{ \begin{array}{ll} \text{Lime} & 32.5\% \\ \text{(CaO)} & \\ \text{Calcium} & \\ \text{Sulphate} & 79.1\% \\ \text{(CaSO}_4\text{)} & \\ \text{Water} & 20.9\% \\ \text{(H}_2\text{O)} & \end{array} \right\} \left\{ \begin{array}{ll} \text{Sulphur} & 46.6\% \\ \text{Trioxide} & \\ \text{(SO}_3\text{)} & \end{array} \right.$$

Standard specifications (ASTM Designation C22-25) state that a material shall not be considered gypsum if it contains less than 64.5 pct by weight of $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$.

Anhydrite, the second calcium sulphate mineral found in nature, may be broken into its constituents as follows:

$$\text{Anhydrite (CaSO}_4\text{)} = \left\{ \begin{array}{ll} \text{Lime} & \\ \text{(CaO)} & 58.8\% \\ \text{Sulphur} & \\ \text{Trioxide} & 41.2\% \\ \text{(SO}_3\text{)} & \end{array} \right.$$

PROPERTIES OF GYPSUM AND ANHYDRITE

Pure gypsum is colorless to white but various impurities change its color to shades of gray, brown, red, or pink. It has a hardness of 2 in the Mohs scale and can be scratched with the fingernail. The specific gravity of pure gypsum is 2.3 to 2.4, so that rock gypsum, free from moisture, weighs about 145 lb per cu ft. Gypsum crystallizes in the monoclinic system in tabular crystals that exhibit good cleavage

* Information for this chapter was freely drawn from Bureau of Mines *Information Circular* 7049 and from the Minerals Yearbooks. The author is indebted also to technicians in the gypsum industry and to the Gypsum Association, Chicago, Illinois, for information used herein.

† National Gypsum Co., Buffalo, New York.

(platy) parallel to the principal plane surface. The compressive strength, as determined by the Bureau of Standards on 6-in. cubes of Virginia gypsum, is:

WEIGHT, PSI	CONDITION
3,224	Dry and loaded on bed faces
2,944	Wet and loaded on bed faces
2,617	Dry and loaded parallel to bed faces

Gypsum is slightly soluble in water, soluble in dilute hydrochloric acid, and insoluble in sulphuric acid. Its solubility in water is increased considerably by the presence of sodium or magnesium chloride.

Gypsum is widely useful because of its peculiar property of losing three fourths of the combined water on application of moderate heat and its ability, when cooled and made plastic by admixture with water, to be spread, cast, or molded to any desired surface or form and finally to resume its original state by "setting." The heating process is known as calcining and the product as calcined gypsum.

Although anhydrite contains no water of crystallization, it is so similar to gypsum that under certain conditions it will change into gypsum; also, under other conditions, gypsum will revert to anhydrite. Anhydrite is commonly white, has a hardness of 3 to 3.5 in the Mohs scale and has a specific gravity of 2.9, so that a cubic foot of anhydrite weighs about 180 lb. Usually it appears compact and granular, although fibrous masses and orthorhombic crystals are found, which have good cleavages. Anhydrite is slightly soluble in water and soluble with difficulty in dilute hydrochloric acid. It is less soluble in water than gypsum but behaves in the same manner.

Another form of gypsum is called gypsite. It is an earthy gypsum containing an abundance of small gypsum crystals scattered through clay or sandy loam and forming up to 90 pct of the mass.

DISTRIBUTION OF GYPSUM DEPOSITS

Gypsum deposits of good quality and commercial size are so widespread in the United States that the development of a deposit depends largely upon the demand for gypsum and its products in the immediate region of the particular deposit. As freight costs are a determining factor, the deposits that are important commercially are in southern California, Iowa, Kansas, Michigan, Nevada, New York, Ohio, Texas, and Virginia. Gypsum is also found in several provinces of Canada, being exported from Nova Scotia and New Brunswick to Atlantic ports in the United States. Gypsum deposits occur in many countries of the world but the United States, France, United Kingdom, Germany, Canada, and the USSR are the leading producers.

POLITICAL AND COMMERCIAL CONTROL

Raw rock is imported by the United States from Canada and Mexico duty free. The bulk of these imports is from wholly owned subsidiaries of United States firms. Any processing of raw rock subjects the finished product to import duties.

PRODUCTION AND CONSUMPTION

Statistics of production for the world are almost nonexistent. However, before the last war, world production was more than 10 million metric tons annually. In the United States, production depends largely upon the amount of building construction and thus fluctuated from a low of 1.3 million in 1933 to 6.2 million in 1947.

PROSPECTING AND EXPLORATION

As commercial deposits of gypsum are widely distributed in the United States, several important factors should be considered before any development work is done. Studies of the potential market and its area and the productive capacity already in the area are necessary to determine whether any new production can be utilized. As previously mentioned, freight costs are an important factor in utilizing a deposit; also, the adaptability of the deposit to low-cost operating methods.

After the economic survey has been completed, the purity and extent of the deposit should be proved by adequate sampling and drilling or trenching to determine the available tonnage of commercial material. Generally one acre of gypsum one foot thick will yield approximately 3000 tons. Exploration drilling usually is performed by a diamond, churn, or air drill.

QUARRYING GYPSUM DEPOSITS

The proper method of development (opencut or underground mining) is determined by the thickness and attitude (flat or inclined) of the gypsum beds, the type and thickness of overburden and the topography of the region. Opencut mining or quarrying is preferred when the gypsum beds are flat-lying or nearly so and have little or no overburden. If the overburden consists of unconsolidated material, such as soil or glacial debris, a greater thickness can be removed economically than if it is consolidated material, such as shale or limestone. This overlying material is removed as far as possible by mechanical stripping (drag-line or shovel), followed by hand stripping to clean out irregularities on the top of the gypsum deposit. The overburden either is cast back onto the quarry floor or is hauled to refuse dumps. In some operations where the cover is light, the overburden and gypsum are shot down together and separated on the quarry floor. Holes for primary blasting are drilled by churn or air drills the full depth of the bench in a line

parallel to and a predetermined distance back of the face. Low-strength dynamite and black blasting powder are the explosives generally used. After the gypsum is broken loose by the primary blast, blockholing or secondary shooting is done to reduce the large blocks to at least one-man size. The broken material is then loaded by hand or mechanical means into cars for transportation to the mill.

Gypsite deposits always lie close to the surface and usually have little or no overburden. As the material is soft and friable, it requires no blasting and is worked with power shovel or scraper.

UNDERGROUND MINING

Where the gypsum beds have a heavy overburden or are inclined so that operations must be carried beneath an increasing thickness of cover, underground methods usually are employed. Underground mining is successful only if the roof is strong enough to require a minimum of timbering. Mine entries are drifts or adits, slopes, or vertical shafts. The room-and-pillar system is common practice on horizontal or slightly pitching beds but steeply pitching beds are worked by the drift and shrinkage-stoping methods. About 75 pct of the gypsum is extracted in the first mining by the room-and-pillar method, which generally is carried to the property limits before any pillars are pulled. Pillar and roof extraction or second mining is carried on the retreat, recovering as much gypsum as possible before the unsupported roof caves. Total recovery should be about 90 pct.

Drills are of two types, an electric-powered rotating drill using an auger bit and a percussion air drill. According to report, undercutting machines are unsatisfactory because the cuttings tend to clog the cutter bars. The rock is broken loose with low-strength dynamite and loaded into mine cars. In vertical-shaft mines the gypsum is raised to the surface by skips, automatic dumping cages, or bucket elevators. In adit or slope mines, it is raised by belt or pan conveyors, or by cable haulage.

PREPARATION FOR MARKET

Between 25 and 30 pct of the gypsum used in the United States is sold in the raw or crude form, as a retarder for portland cement, fertilizer, fillers for paper textiles, and other purposes, and as a fluxing agent. The crude gypsum is prepared for these uses by crushing to specified sizes and screening, if desired.

The remainder of the tonnage sold, representing 94 pct of the value, requires calcination for the following uses:

1. Molding, casting, pottery plasters.
2. Dental plasters.
3. Metal-casting plasters.

4. Building materials: (a) plasters, (b) Keene's cement, (c) board products, (d) tiles and blocks.

Processing

Modern preparation of gypsum for manufacture into calcined products may be divided into the following stages: Crushing and grinding, calcining, regrinding, and mixing. Most of the machinery used is standard and is not designed primarily for the gypsum industry. The machines especially adapted to gypsum processing are the calcining kettles and the feeding and conveying equipment for finely ground and calcined gypsum. However, the physical character of gypsum varies from place to place and care must be taken to select the most suitable equipment.

Crushing and Grinding

In recent years, crushing and grinding machines have been perfected to eliminate much of the preliminary crushing of man-sized rock. Impact mills, such as the swing-hammer or rigid-hammer type and ring-roller crushers, are used successfully where primary crushed rock does not exceed 6-in. size. These mills reduce this material to minus $1\frac{1}{2}$ -in. or smaller, which is suitable size of feed for rotary kilns. Fine-grinding machines have been improved so that they handle larger feed and reduce it to smaller size than formerly. Buhrstones and emery mills, which in the past were favorites for fine grinding in the gypsum industry, are rapidly being discarded for the more efficient, high-capacity modern mills.

A combination drying and grinding mill, which is used to some extent in certain industries, has been tried in the gypsum industry and appears to have possibilities. This mill, which is directly connected with an air separator, may also utilize the waste heat from the calcining process and dries, calcines, and grinds the crude gypsum in one operation.

Little trouble is experienced in conveying and elevating crude gypsum with standard handling equipment. However, for the more finely ground product, screw and drag-chain conveyors are generally used to convey and feed the material to the bins or calcining kettles.

Calcining

The calcining process, accomplished by kettle or rotary kiln in a gypsum plant, is the stage during which part of the water of crystallization is removed from the raw gypsum and the hemihydrate is produced.

KETTLES

Calcining kettles are peculiar to the gypsum industry. They consist of a cylindrical steel shell $\frac{3}{8}$ to $\frac{1}{2}$ in. thick, having a diameter of 8 to 15 ft and a depth of 6 to 14 ft. Popular sizes are 10 by 8, 10 by 10, 12 by 10, and 14 by 12 ft. The bottom of the kettle is a one-piece, convex, steel plate 1 to 3 in. thick, placed so that the convex surface is inside the kettle. Sectional bottoms made by bolting together 6 to 15 triangular segments are not as satisfactory as one-piece bottoms except in the larger kettles. On the top or cover plate, there is a trap for changing raw gypsum and a vent pipe to conduct the dust and evolved steam to a dust collector. For efficient heating, horizontal flues 8 to 14 in. in diameter extend through the kettle from side to side. Usually there are four flues, arranged in parallel pairs, one above the other or set in one plane. To prevent overheating, the gypsum is agitated constantly by horizontal rabble arms or sweeps attached to a vertical gear-driven shaft in the center of the kettle. Two sets of rabble arms are commonly used, one equipped with drag chains below the flues near the bottom and the other just above the flues. The discharge gate or spout of the kettle is at the bottom of the side wall.

The kettle is set over the firebox, resting on a heavy iron lip ring which is supported on a firebrick foundation. The firebrick masonry extends upward and surrounds the kettle, leaving an annular space of 12 to 16 in. between the brick and the kettle shell. This flue space is provided with baffles that direct the heat, applied at the bottom of the kettle, around the shell and through the horizontal flues before it passes out of the stack.

A hot pit is built directly under the discharge spout of each kettle. It is constructed with a sloping bottom so that the calcined gypsum will flow freely to the screw conveyor at the lower side of the pit. The hot pit has a well-fitted cover in which a flue permits the escape of steam, thus preventing condensation in the pit.

In the kettle process, finely ground raw gypsum is run continuously through the charging gate until the kettle is full. Loading requires from 20 to 45 min. and is done directly after the kettle has been emptied of its previous charge. During loading, the kettle temperature drops from about 170°C (340°F) to approximately 110°C (230°F). The temperature then rises slowly to 120°C (250°F), at which point the gypsum appears to boil vigorously and emits steam rapidly. This apparent boiling is caused partly by mechanical agitation of the rabble arms but chiefly by released water of crystallization in the form of steam, which, as it escapes upward, tends to float the fine particles of gypsum. The temperature remains virtually the same until the boiling becomes more

subdued, then rises at an increasing rate. Between 150° and 165°C (300° and 330°F), boiling ceases, little or no steam is given off, and the contents of the kettle have settled to 10 to 14 pct less than the original volume. This quiet period indicates that most of the gypsum particles are dehydrated to the hemihydrate. Heating is continued until the contents of the kettle register about 170°C (340°F), at which temperature they are discharged into the hot pit. The discharge temperature at different mills ranges from 160° to 175°C (320° to 350°F).

Calcined gypsum at this stage is known as "first-settle" calcined gypsum. It contains from 5 to 6 pct water and is employed for wall plasters, board, block, and most of the common uses of calcined gypsum. The time required to calcine a kettle of raw gypsum to first-settle plaster ranges from 1 to 3 hr, depending chiefly on the rate of firing, the fineness and purity of the raw gypsum, and the kettle size and design.

To obtain "second-settle" calcined gypsum, the kettle contents are heated beyond the first-boil and first-settle stages. At about 380°F, the gypsum again starts to boil and give off steam. This second boil is of shorter duration and less vigorous than the first boil because a smaller percentage of water of crystallization is removed. The product, which contains less than 1.5 pct water when fresh, is known as second-settle calcined gypsum. This material has less plasticity but greater density and strength than first-settle plaster. At present, little second-settle calcined gypsum is manufactured because material with the same qualities is obtained by specially treating first-settle calcined gypsum as explained later, in the paragraph on aging plasters.

The procedure for calcining gypsite in kettles differs somewhat from that for calcining rock gypsum, because of the impurities and high free-moisture content of the gypsite. Charging is done slowly in batches of $\frac{1}{4}$ to 1 ton with enough time between batches to allow the material in the kettle to reach the first-boil stage. This process, which prevents the agitators from sticking, is continued until the kettle is full. A long period of calcination (3 to 8 hr) is required for gypsite. In discharging, it is customary to leave a prime of $\frac{1}{2}$ to 1 ton of calcined gypsite in the kettle to protect the hot kettle bottom from the wet raw charge.

In the kettle process, accurate control of calcination is maintained by means of recording thermometers. Firing rates are closely controlled at modern plants with oil, gas, or coal stokers.

As kettles are adaptable to the calcination of all types of rock gypsum and gypsite, they are used in all sections of the country and are the principal type of calcining equipment. In 1946, there were 142 kettles in operation in the United States.

ROTARY KILNS

The modern type of rotary kiln is similar to that used for burning portland cement and lime. In the gypsum industry, it consists of an end-fired cylindrical tube 70 to 155 ft long and 6 to 8 ft in diameter. The more recent installations are near the maximum length and diameter given. The kiln, which is supported with a slight pitch, is fed from the high end. Inside the kiln, spiral flights are provided in the first 10 ft at the feed end, to prevent the feed from piling up and spilling over the end. Low, longitudinal diaphragms for about one third to one half of the length break up the rock stream and prevent stratification or segregation of the rock according to size. The kiln is lined with firebrick at the firing end for one fourth to one third of its length.

As gypsum calcination is, relatively, a low-temperature process, an outside combustion chamber usually is used at the end of the kiln, the draft being regulated to carry the hot gases into the kiln counter to the flow of the rock. The rotary kiln may be fired from either end but standard practice is to fire from the discharge end of the kiln to effect a counterflow of gypsum and hot gases. This arrangement is more efficient with regard to fuel consumption than the parallel-flow method of firing from the feed end of the kiln.

Rock gypsum for rotary-kiln feed is crushed to about $1\frac{1}{4}$ in. or smaller. Preferred practice is to size this material further by removing the fines, although some plants make no separation by sizes after crushing. The gypsum passes through the kiln in approximately 45 min. and is discharged at a temperature of 160° to 195°C (320° to 380°F), counterflow firing. In the early installations, the kilns discharged into hot pits, where final calcination of the large fragments took place. Present practice is to send the discharge directly from the kiln to grinding mills, where the calcination is completed.

The quantity of dust picked up by the hot gases depends upon how heavily the kiln is forced and whether or not the fine material is removed from the raw feed. In natural-draft kilns a simple dust chamber at the base of the flue stack recovers most of the dust, which may be returned immediately to the kiln discharge.

Temperature in the rotary kiln is controlled by two pyrometers, one in the flue gases as they leave the kiln and the other in the discharge stream of calcined gypsum.

This type of kiln, with its high capacity, low labor costs, low grinding costs and relatively low fuel and power requirements, is widely used on gypsum mined in New York and on imported gypsum. It has also been adapted successfully to the softer gypsum of the Middle West and to high-temperature calcination of gypsum to produce material suitable for the manufacture of Keene's cement.

BEEHIVE KILNS

The only other type of gypsum-calcining equipment employed in the United States at present is a beehive kiln used for the manufacture of Keene's cement. It consists of a circular base 20 to 30 ft in diameter, surmounted by a low dome that makes the kiln 12 to 16 ft high. The kiln is heated by several furnaces or combustion chambers, which are operated independently. The hot gases are conducted to the top of the kiln by flues on the inner wall, then down through the gypsum and out of the kiln by flues and an underground conduit to a stack. Selected lump rock gypsum 6 to 10 in. in diameter is heated at white heat for 3 to 5 days, after which the calcined lumps are crushed, ground, screened, and pulverized.

Fuel used in the various types of gypsum-calcining equipment may be coal, fuel oil, or natural gas, depending upon which will furnish the greatest heat (Btu) for the lowest cost. When coal is used in end-fired rotary kilns, it is usually pulverized and injected into the combustion chamber by an air current.

REGRINDING

Calcined gypsum, obtained by kettle calcination, is in a pulverized condition when discharged into the hot pit. It is removed from the hot pit by screw conveyors as soon as possible because hot-pit storage accelerates the set, lowers the plasticity and water ratio, and increases the density of first-settle plaster. After the calcined gypsum leaves the hot pit, it passes over a vibrating screen, from which the undersize goes to the mixing plant and the oversize is either reground or returned to the kettle feed. In some plants, the hot-pit discharge is not screened or reground but is conveyed directly to storage bins or to the mixer.

Calcined gypsum discharged from rotary kilns is sent directly to regrinding mills (swing-hammer, roller, or buhrstone). In these mills, calcination of the larger fragments of calcined gypsum is completed and the material is thoroughly mixed to yield a product of uniform quality and characteristics. The discharge of the regrinding mills may be screened and treated in the same way as kettle-calcined gypsum or it may be sent directly to the mixing plant.

The regrinding of calcined gypsum in tube mills was begun about 1911 but was not generally accepted until after 1929. Tube milling increases the bulk, plasticity, and sand-carrying capacity of calcined gypsum. With the Emley plasticity machine, it has been found that the plasticity of calcined gypsum before tube milling (150 to 180) can be increased to between 250 and 350 by tube milling. This type of regrinding is widely used on all ordinary wall plasters in which high bulk, plasticity, and sand-carrying capacity are desirable. Usually it

is not applied to calcined gypsum that is intended for manufacture of gypsum board or block or certain specialty plasters. Tube-milled plaster will not mix readily or uniformly with lime putty and should not be used for gauging plaster.

The rate of feed should be constant and may be determined roughly as one ton of calcined gypsum per hour for every two tons of balls in the mill. Balls of $\frac{3}{4}$ to $1\frac{1}{8}$ -in. diameter appear to be most effective.

AGING PLASTERS

Plasters that require a minimum of water for mixing and setting are desired for casting, molding, gauging, dental, and orthopedic uses. These products are less plastic but denser than the common gypsum plasters, have greater strength, and have a minimum of voids in the set product. Formerly second-settle calcined gypsum was used to obtain the desired properties but in present-day practice the same qualities are obtained by aging or treating first-settle material. To age calcined gypsum, it is only necessary to expose the material to air for a certain period of time. Artificial aging is accomplished by introducing a predetermined quantity of a chemical salt, such as calcium chloride, into the kettle during calcining. This process affords close control of the degree of aging and is said to yield a more uniformly aged plaster than natural processes.

MIXING

Calcined gypsum for wall plasters is delivered to the mixing plant, where it is mixed in 1 to 2-ton batches with additives to control the rate of set. For plastering of interior walls of buildings of all types, fiber may be added.

Calcined gypsum for the manufacture of boards and blocks is usually mixed continuously with water. Accelerator is added as needed to control the set in relation to machine speeds of manufacture.

TESTS AND SPECIFICATIONS

Because of the many varied products produced from gypsum, the tests and specifications are too numerous to list in a publication of this size. Full specifications on all products can be obtained by writing to the Government Printing Office, Washington, D. C.

MARKETING AND USES

Sales of gypsum products for building uses accounts for approximately 90 pct of the total industry; thus the markets for gypsum products follow very closely the building market. Statistics published by the F. W. Dodge Corporation are very useful in determining the relative importance of the various markets. Gypsum for building material is usually sold on an f.o.b. price plus freight from the nearest produc-

ing mill, therefore the plant location in relation to the market to be served is a very important factor. Sales are most always made to a lumber or masonry supply dealer and not direct to the contractor or ultimate user. In some cases, sales are made to Government agencies.

Uncalcined gypsum sold for industrial uses and agricultural purposes totals approximately 6 pct of the industry. These materials are low-price items and cannot absorb high freight charges, therefore sales are limited to very small areas. Sales of agricultural gypsum are confined to areas where the material is required for control of soil conditions; for instance, the southeast and west coast of the United States. Sales are seasonable, depending on the crop-growing season. Most of these products are sold on the basis of chemical analysis, thus eliminating some producers from this market.

TABLE 1—*Prices of Gypsum and Products, United States^a*

Year	Cement Retarder, per Ton	Base-coat Plasters, per Ton	Lath, per M Sq Ft	Wallboard, per M Sq Ft
1937	\$1.90	\$ 9.02	\$13.00	\$21.67
1938	1.84	8.91	12.71	21.31
1939	1.81	9.03	12.84	21.61
1940	1.95	8.82	12.54	21.57
1941	2.00	8.81	12.76	21.88
1942	2.04	8.95	12.63	22.18
1943	2.11	8.95	12.47	21.98
1944	2.10	8.96	12.64	21.94
1945	2.26	9.53	13.64	22.53
1946	2.60	10.68	16.17	22.99
1947	3.31	10.89	18.87	26.07

^a Source: Minerals Yearbook.

Calcined gypsum is sold to industrial users also, in amounts approximating 4 pct of the total sales of the industry. The bulk of these industrial plasters are for use in casting and molding, pottery, plate glass, orthopedic, and dental purposes. The chemical analysis is a limiting factor and specifications for each use are closely controlled, requiring special products not used in any quantity by other industries.

Sales to industrial users require definite shipping schedules, as these users do not buy for stock but for consumption in relation to the rate of production.

Industrial gypsum products in small quantities are sold through dealers or distributors and in large quantities may be sold directly to the user. Agricultural gypsum, however, is usually sold to agricultural supply houses.

As most industrial uses are of a technical nature, they require spe-

cial assistance of factory representatives. This is a service that most dealers or distributors of gypsum products for the building trade are not able to render.

PRICE HISTORY

Prices of gypsum products remained steady for the period from 1937 through the end of the Office of Price Administration, when price increases were effected. The largest price increase, from 1939 to 1947, was for crude gypsum as sold for cement retarder. The increase was from \$1.81 per ton to \$3.31 per ton, or 82.9 pct. Table 1 shows prices from 1937 to 1947 for crude gypsum, base-coat plasters, lath and wall-board.

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CHAPTER 21

HEAT AND SOUND INSULATORS*

BY J. E. LAMAR† AND J. S. MACHIN‡

INSULATING materials include a wide variety of nonmetallic mineral products such as exfoliated vermiculite, expanded gypsum, 85 pct magnesia, diatomite, asbestos, perlite, cellular glass, pumice, silica aerogel, expanded aggregates and mineral wool. Except mineral wool, most of these products, or the materials from which they are manufactured, are described in other chapters of this book.

PROPERTIES OF INSULATING MATERIALS

The insulating properties of the materials considered in this chapter result in general from entrapping extremely small pockets of air in such a manner that heat is not transferred by convection. The minimum heat conductivities of such insulating materials are slightly greater therefore than the conductivity of still air. In addition, conductivity varies with the overall density of the material, the temperature range in which the measurements are made, and the form into which the material is fabricated. However, the numerical value of heat conductivity should not be the sole criterion of an insulating material; for a particular application it may be advantageous to use a material of somewhat higher conductivity in order to secure other desirable engineering properties. This is especially true with certain materials that are used because of their refractoriness.

Comparative insulating values of some commonly used insulating materials are shown in Table 1. In comparing the values presented in this table it should be borne in mind that heat conductivity varies with the mean temperature, with the overall density, and with the amount of moisture present. With fibrous or granular materials it varies with fiber or grain size and with the amount and kind of binder, if any is used. Under some circumstances it may vary with the arrangement of

* This paper is a revision of the chapter of the same title by J. E. Lamar and Charles F. Fryling that appeared in the first edition of *Industrial Minerals and Rocks*, AIME, 1937. Published by permission of the Chief, Illinois State Geological Survey.

† Geologist and Head, Industrial Minerals Division, Illinois State Geological Survey, Urbana, Illinois.

‡ Chemist and Head, Industrial Minerals Division, Geochemical Section, Illinois State Geological Survey.

the fibers or grains and with the position of installation; that is, whether it is horizontal or vertical. For graphic treatment of some of these factors see references 32, 37, 38 and 70.

Sound-insulating materials^{1,40,80} serve two purposes, to absorb sound and to reduce its transmission. Sound-absorbing products are used to improve the acoustics of theaters, churches, and other public buildings and usually are employed in the form of porous tile, block, or plaster. Unlike heat-insulating materials, which depend for their insulating properties on the presence of numerous small air pockets, sound-absorbing materials owe their properties to the existence of channels with which are connected many small pores. The sound waves are admitted to the insulating material by the channels and are trapped by the pores, where ultimately they are dissipated in the form of heat.

The reduction of the amount of sound transmitted through walls,

TABLE 1—*Heat Conductivities of Various Insulating Materials*

Material	Reference	Density, Lb per Cu Ft	Mean Temperature, Deg F	Conductivity <i>K</i> ^a
Concrete—pumice aggregate.....	37	65	75	2.42
Concrete—expanded burned clay aggregate..	37	59.9	75	2.28
Cellular concrete.....	37	50	75	1.44
Cellular concrete.....	37	70	75	2.18
Concrete—expanded vermiculite aggregate...	37	50	90	1.1
Concrete—expanded vermiculite aggregate...	37	20	90	0.68
Glass-wool fibers 0.0003 to 0.0006 in. in diameter.....	37	1.5	75	0.27
Fibrous material made from dolomite and silica (mineral wool).....	37	1.5	75	0.27
Fibrous material made from slag (mineral wool).....	37	9.4	103	0.27
Mineral wool, granulated, machine-blown. Horizontal position, no covering.....	37	5.74		0.30
Rock wool (loose).....	38	6	100	0.27
Rock wool felted between wire mesh.....	38	16.6	100	0.283
Rock wool, felted blanket.....	77	8.2	300	0.41
85 % magnesia, 15 % asbestos slab.....	37	19.3	86	0.51
Foamglas.....	69	10.5	50	0.45
Foamglas.....	69	10.5	300	0.70
Vermiculite, expanded.....	70	8	100	0.48
Diatomite powder.....	70	10.6	86	0.31
Still air.....	77	0.08	32	0.156
Kaolin insulating brick (recalculated).....	72	27	932	1.2
Kaolin insulating brick (recalculated).....	72	27	2100	3.1

^a Conductivities *K* expressed in British thermal units per hour per square foot per degree Fahrenheit per inch thickness.

partitions, or other barriers is accomplished principally by reflecting the sound by means of dense, smooth-surfaced tile, block, or plaster. Sound-absorbing materials may be used also to aid the process by reducing the incident sound.

Usually the manner of fabrication of the various nonmetallic minerals used for sound insulation is more important than the character of the raw material itself. As a general rule, however, it may be said that fibrous or cellular nonmetallic minerals that are good heat insulators can be converted by proper methods of manufacture to products of value for sound insulation.

Data available regarding the efficiency of nonmetallic minerals as sound insulators refer chiefly to the diverse products in which they are used, and are of little importance from the standpoint of raw materials because the method of manufacture largely influences their properties.

INSULATING MATERIALS

Asbestos—The term “asbestos” is used commercially to describe any mineral that can be separated readily into more or less flexible fibers (p. 43 of ref. 41 and ref. 11). All the commercial varieties of asbestos are either amphibole or chrysotile, the latter being the most useful variety.¹¹ As an insulating material the usefulness of asbestos depends to a considerable degree on its incombustibility, its fibrous structure, and the flexibility of the fibers that permits it to be woven into fabrics (p. 62 of ref. 41). (See chapter 2 of this volume.)

Asbestos is used for heat insulation as fiber and also in various manufactured forms such as yarn, cordage, wick, tape, cloth, blankets, paper, boards, and blocks. Asbestos cements made of short-fiber asbestos and a binder are used extensively as pipe and boiler coverings (p. 8 of ref. 11 and pp. 129–130 of ref. 67). Asbestos felt, cloth, and plaster containing asbestos are used for acoustic work.⁶⁷

Basic Magnesium Carbonate—Basic magnesium carbonate (see chapter 24) is made chiefly from dolomite, by a chemical process that involves calcination of the dolomite followed by slaking to give calcium and magnesium hydroxides. These hydroxides, when treated with carbon dioxide in the presence of water, yield the relatively insoluble calcium carbonate and the soluble magnesium bicarbonate. The latter is separated from the calcium carbonate by filtration and recovered from solution by boiling, which converts it to the relatively insoluble basic magnesium carbonate (p. 205 of ref. 41). This carbonate is used in the manufacture of pipe and boiler coverings for heat insulation. The product “85 pct magnesia” widely used for pipe covering is composed of about 85 pct of basic magnesium carbonate and about 15 pct of asbestos fiber.

Diatomite—Diatomite^{21,22,57} (see chapter 13) is used for heat and cold insulation as brick, block, aggregates, powders, and cements. The brick are sawed from the diatomite deposits or are fabricated with or without a binder. Aggregates and powders are made by crushing and pulverizing raw diatomite and, with the addition of suitable bonding materials, are employed to make a variety of insulating products. For sound insulation of buildings and homes, diatomite powders, granules, blocks, sheets, and the like are used.

Gypsum—Calcined gypsum^{13,19,55,58} is used for making tile or blocks that have a cellular structure and are employed for low-temperature heat insulation and for acoustic insulation. These products are made by including in a mixture of calcined gypsum and water certain chemicals that produce gas and thus froth the mixture. Other types of heat or sound insulating materials made from calcined gypsum, or from calcined gypsum in combination with other materials, include insulating and acoustical plasters, various types of boards and blocks and a granular product for pouring into spaces to be insulated.

Pumice and Pumicite—Crushed pumice^{14,36} is used in plaster and stucco for sound insulation but is not known to have been used for heat insulation, although a massive bed in California is said to furnish material that can be cut into blocks for insulation of refrigerators.⁹ Pumicite, also called volcanic ash, is used to a limited extent as a heat insulator.

Vermiculite—Vermiculite^{12,65} is a mica that expands or exfoliates when heated into tabular masses composed of numerous thin sheets (see chapter 26). It is used as loose granules for insulation of houses, ovens, driers and the like. With the addition of suitable binders, it is formed into sheets, blocks, bricks, and pipe coverings having a wide variety of insulating uses. Insulating cements are made from expanded vermiculite and a binder. Vermiculite plasters are employed for both heat and sound insulation.

Perlite—Perlite,^{2,64} or pearlite as it is sometimes called, is a term applied to a siliceous or acid lava containing 2 to 5 pct included water. Typically it is a rhyolitic material. Quick heating to the softening point causes puffing or bloating of the material as a result of the conversion of the included water into steam. By varying the firing conditions, the physical properties of the puffed product can be controlled to some extent. The exterior of the expanded granules may be sealed by briefly exposing them to a temperature above that required for puffing. As a commercial product, perlite is relatively new but it appears to be suitable for a variety of heat and sound insulating purposes both as puffed granules or in otherwise processed and fabricated forms.

Cellular Glass—Cellular glass,⁷ also known by the trade name of "Foamglas," is made by melting in a suitable mold an intimate mixture

of finely pulverized glass and a small amount of gassing agent. The gassing agent in Foamglas is said to be "pure carbon";⁶⁹ more exactly described gassing agents are calcium carbonate and carbon black,⁶⁰ which may be the "pure carbon" just mentioned. When the glass melts it is bloated by the gas evolving from the gassing agent and at the same time fills the mold. The resulting product is a light-weight glass containing many small sealed pores. It is trimmed or sawed into blocks and slabs, which are used as thermal insulation.

Silica Aerogel—Silica aerogel^{8,59,82} is a light-weight thermal insulation having pores of submicroscopic size. It is made by mixing solutions of sulphuric acid and sodium silicate to form silica aquagel. Alcohol is then substituted for the water in the aquagel to produce an alcogel from which the alcohol is eliminated by a suitable process to give the porous aerogel. As the aerogel offers small resistance to the transfer of radiant heat at elevated temperature, an opacifier, such as finely ground silicon, may be added to overcome this condition.

Mineral Wool—See subsequent detailed discussion.

Other Insulating Materials—A number of other products having a porous or cellular structure find use as insulation. Brick of this type made from plastic fire clay are used for high-temperature insulation. Their porous structure results from the "addition of a combustible, removed in the firing; addition of a volatile, which is driven off in drying; use of a combination of the volatile and combustible; and by chemical bloating."¹⁶ Most manufacturers employ a combustible.¹⁶ Light-weight aggregates^{12,25,39,56} made from clay bloated during firing, slag, or cinders, as well as some of the porous or cellular materials previously mentioned, including pumice and vermiculite, are used for making light-weight concrete, which, although employed primarily as a structural material, also has heat and/or sound insulating value. Light-weight aggregates may also serve as low-conductivity fillers.¹⁵ Another type of porous concrete having insulating properties is made by incorporating in the concrete mix gas-producing compounds that foam the concrete.¹⁵ Fire-clay brick and other special types of brick, certain kinds of stone, and various other refractory materials also serve as heat insulation in the broad sense of the term.

MINERAL WOOL

Mineral wool is an artificial product composed of extremely thin fibers of silicate glass, mostly 1 to 10 microns in diameter, and derives its name from its resemblance to sheep's wool. It is widely used for insulation and owes its insulating properties to innumerable minute air pockets, which are entrapped by the fibers of the wool and prevent the transfer of heat by convection and likewise serve to trap and dissipate sound waves. The term "mineral wool" has been used and still is used

to include rock wool, slag wool, glass wool, glass silk and silicate cotton. In general, the names indicate the raw material from which the wool is manufactured. However, at present it appears that the usage of the term mineral wool is undergoing a change to the extent that it is used to designate only slag and rock wool whereas glass wool and fiber are considered to be in a separate category. The term "rock wool" was applied originally only to mineral wool made from natural rock but the term is now used commercially to include also wool made from slag.⁶ Probably this has resulted at least in part from the fact that manufacturers of mineral wool who originally used rock as a raw material and called themselves "rock-wool companies" have since changed to slag as a raw material without altering the company title to indicate the change.

In the following discussion the use of three categories, rock wool, slag wool and glass wool, is adhered to for clarity and convenience.

Manufacture of Mineral Wool

The production of fiber is fundamentally the same for all types of mineral wool and involves subjecting a molten material, usually a silicate of glassy nature, to shearing and/or tensile forces that draw it out into fibers. The fibers are cooled simultaneously at such a rate that their temperature drops below the softening point very quickly after they are formed. The process may be carried out in such a manner that a continuous unbroken fiber is formed or, by different methods of applying the force, a great number of relatively short fibers may be produced. When continuous fibers are desired, the usual method is to draw out thin streams of the molten material into fibers by winding them on a rotating drum or spool, so controlling the process that the fiber attains the proper size and temperature by the time it reaches the drum. If a mass of more or less interlaced fibers is required, the usual procedure is to subject a stream of the molten material to the action of a blast of steam or compressed air that has sufficient velocity to disintegrate the stream and cause the droplets to be spun out more or less completely into fibers. A more recently developed method of attenuating the molten material into fibers, which has been called the spinning process,^{63,66} breaks the melt into fibers by means of a spinning disk. Only materials that do not devitrify readily are suitable for making useful fibers.

GLASS WOOL

Glass wool, glass silk, fiber glass, or silicate cotton, as it has been variously called, is commercially made by at least two processes. Descriptions in the literature of both processes are incomplete, possibly because some of the details are manufacturing secrets.

In one process the molten glass from the melting tank flows through

small openings in a plate. These small streams of molten glass are blown by jets of compressed air or steam into fibers, which are collected as a blanket on a traveling belt. The principal operating variables are the batch composition, the temperature and the velocity of the air or steam jet. It has been reported that these velocities are of the order of 72,000 fpm and the temperature of the molten glass 2800°F.²⁴ The design of the plate through which the streams of molten glass issue is most important. Since it is essential that the streams be uniform if the product is to be uniform, it is also essential that the plate be made of a material that will prevent the openings from changing greatly in size with use. These considerations have made alloyed platinum the favored material for the plate.

Another process is used for making continuous fiber. In this, the furnace is small and is electrically heated. The streams that issue from small holes in a plate (as in the first process described) are attenuated by being wound on spools that are rotated at peripheral speeds of the order of 5000 to 10,000 fpm, controlled to give filaments of the desired size. The furnace is fed with glass spheres about $\frac{5}{8}$ in. in diameter. The fibers commonly made by this process are finer than those made by the blowing process and are used as heat insulators only for special applications.

The product made by the blowing process resembles mineral wool in appearance but is nearly shot free. The average diameter of the fiber is considerably greater than that of most commercial rock or slag wool. The length of the fiber is also much greater and consequently the material is more resilient than rock or slag wool. As sold, the density is ordinarily less than half that of the corresponding rock-wool or slag-wool product.

ROCK OR SLAG WOOL

The most commonly used process for making rock or slag wool involves melting pieces of the batch material in water-jacketed cupolas. The cupola dimensions range from 2 to 6 ft in diameter and from 7 to 16 ft in height; the water-jacketed part of most cupolas is in the range 8 to 10 ft high. The fuel used is coke. The quantity of coke required varies from $\frac{1}{3}$ or $\frac{2}{3}$ of the weight of raw rock materials to $\frac{1}{6}$ of the weight of some of the most suitable raw slag materials. At a few plants, reverberatory furnaces fired with oil or gas are used.

A plant that melts slag in an electric furnace of the induction type was recently reported. One Canadian plant has produced wool on a commercial scale using the electric-arc furnace for melting.

The reverberatory and electric furnaces, induction or arc type, have an advantage in that they can handle relatively small batches of material, which permits closer control of the composition. The most seri-

ous weakness of the hearth-type furnace is that its refractory parts are susceptible to the corrosive action of the melts that are commonly used for making wool.

The stream of molten material as it issues from the furnace is in most plants divided into smaller streams before it is blown or spun into fibers. Other factors being equal, smaller streams are more completely converted into wool by the blowing process.

The character of the wool (fiber diameter, fiber length, shot content, and other factors) is affected by batch composition, blowing temperature, pressure drop at the blowing nozzle, and various features of equipment design. Although the practice varies from plant to plant,⁷⁵ in many minor ways the process is basically the same in nearly all plants.

A notable exception is a Canadian plant that has produced a long-fibered high-quality wool, which commanded a premium price, by the spinning disk process.^{17,66} In this process most of the shot are thrown out of the wool by centrifugal force during the spinning. Another plant that might be considered an exception is described by Thoenen.⁷⁵ It uses a rotating disk to break up the slag stream and project the droplets into the steam jet.⁸¹

The improvement in quality of mineral wool, which has been considerable over the past 10 years in this country, has been brought about by more careful control rather than by basic change in the process.

Materials for Making Mineral Wool

The chemical analyses of slags, woolrocks, and mineral wools shown in Table 2, as well as many others that may be found in the literature, indicate to some extent the rather wide compositional range of materials that may be used for making wool. The four major components of most commercial wools are silica, lime, alumina, and magnesia, although some wools have been reported in which the iron content as FeO runs as high as 30 pct.⁷⁵ The typical silica content ranges from 36 to 45 pct.

The silica varies less from plant to plant than any of the other major components. Alumina ranges from 5 to 20 pct and the sum of the silica and alumina varies usually between 48 and 55 pct. Lime in most wools ranges from 30 to 40 pct and magnesia between 5 and 15 pct. In addition, miscellaneous oxides such as Fe_2O_3 , P_2O_5 , ZnO and PbO , alkalis, and other minerals, may be present in varying but usually small amounts. These figures are approximate and are to be regarded as dictated in a given plant by the materials available and the operating conditions and not in any way as setting limits outside which wool cannot be made successfully. Laboratory studies by Fryling²⁶ indicate that it is possible to produce wool from the four oxides mentioned above

with melting temperatures of 1500°C and lower, inside the following compositional limits: SiO_2 , 35 to 65 pct; Al_2O_3 , 0 to 33 pct; CaO , 5 to 50 pct; and MgO , 0 to 32 pct.

GLASS WOOL

Little specific information is available on the composition of the glass used in making glass wool or glass fiber. The glass is variously described as "high-quality glass,"⁷³ "ordinary commercial glass,"⁷¹⁸ "soda-lime glass,"⁷²⁶ and "special borosilicate glass."⁷²⁴ Schoenlaub⁷¹ describes a composition for making glass fiber that fits the latter description and that has the composition CaO , 16 to 19 pct, MgO , 3 to 6 pct, Al_2O_3 , 12 to 16 pct, SiO_2 , 52 to 56 pct, and B_2O_3 , 9 to 11 pct. Presumably the raw materials are those commonly used in making various other types of commercial glasses, which are described in standard works on glass technology.

SLAG WOOL

In recent years iron-blast-furnace slag has become the most used raw material for making mineral wool. Lead⁷²³ and copper slag⁷⁴⁵ also have been used, as has slag from the reduction of pebble phosphate.⁷⁹ Except in special situations, it is cheaper to produce mineral wool from slag than from calcareous or argillaceous rock. This statement, of course, assumes that the composition of the slag is such that excessive additions of calcareous or siliceous materials are not required to bring the slag within the desired compositional limits. The greater amount of wool produced per ton of cupola feed when slag is used rather than rock increases cupola capacity. This fact, coupled with saving of fuel required to drive off volatile material from rocks, and also usually greater uniformity of composition of slag as compared with rock, has led to increased use of slag.

Some slags have compositions suitable for blowing into wool without addition of any other material. More frequently the composition is adjusted by relatively small additions of siliceous or calcareous material. Materials that have been used for these additions are granite, quartzite, sandstone, gravel, shale, fluorspar, old brick, limestone, dolomite, and slags of different compositions.

ROCK WOOL

Rock wool can be made from two general classes of raw materials: natural woolrocks and rock mixtures or composite woolrocks. Both the natural woolrocks and composite woolrocks are composed dominantly of lime, magnesia, alumina, silica, and carbon dioxide, although it has been shown that neither alumina nor magnesia is essential.²⁶ Experiments indicate that in general rocks or rock mixtures containing between 20 and 30 pct carbon dioxide, or roughly 40 to 65 pct calcium

carbonate or calcium and magnesium carbonates, and the rest chiefly silica and alumina, will make rock wool if properly processed. Table 2 lists typical analyses of woolrocks and rock wools.

Natural woolrocks and rock mixtures, or composite woolrocks, are of two kinds, consolidated and unconsolidated. It is important that the former yield a minimum of "fines" or small rock fragments in the process of quarrying and crushing, because fine materials tend to obstruct the free passage of air and heat through the cupola, thus reducing its efficiency, or are blown out by the air blast. The fact that un-

TABLE 2—*Chemical Analyses of Typical Woolrocks, Rock Wools, Slags, and Slag Wools*

Material	Reference	Composition, Pct						
		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Ignition Loss	S
Woolrock:								
Illinois.....	26	29.76	7.95	2.82	12.21	17.74	27.15	2.37
		28.86	7.39	2.14	13.60	17.15	28.20	2.86
		37.25	3.21	1.12	2.30	30.37	25.48	0.27
Indiana.....	46	23.92	8.00		12.34	21.48		
		28.08	8.64		12.18	19.90		
Slag:								
Wisconsin....	74	38.0	11.0	1.0	19.0	28.0		0.5-0.8
Slag.....	74	38.4	10.5	0.7	15.3	31.5		1.6
Slag.....	79	48.74	1.27	0.36		43.76		2.25 ^b
Rock wool:								
Indiana.....	46	36.40	12.16		18.77	32.67		
Indiana.....		34.07	11.19		10.57	44.08		
Slag wool:								
German.....	34	34.0	9.1	2.7	6.2	38.7		9.3 ^c
American....	26	39.5	37.6		7.0	15.1		0.8
American....	26	36.3	13.1	20.4 ^a	2.4	27.2		0.6

^a Probably exists in slag as FeO.

^b P₂O₅.

^c Includes MnO, 4.7 pct; CaS, 3.8 pct.

consolidated materials produce fines is probably not important and they may even be desirable, as these materials generally require pre-cupola consolidation. This may be effected by various means, such as sintering, the use of cementitious or binding materials, or forming by pressure.

As the properties of rock wool are closely related to the chemical composition of the raw material from which it is made, it is desirable that woolrock deposits be of uniform character. Likewise, uniformity of raw materials for mixtures or composite woolrocks is important. Natural sedimentary woolrocks made up of a single type of rock, although variable in composition, are thought to be somewhat less variable

as a rule than those composed of interbedded unlike rock strata, because the beds of the latter are often of variable thickness.

In 1939, a survey of 13 rock-wool plants⁷⁵ revealed a wide variety of materials in use, including: impure dolomite; calcareous shale and sandstone; limestone, dolomite, and sandstone; old firebrick, dolomite, limestone, fluorspar, and other combinations of earth materials. Other mixtures mentioned as rock-wool raw materials are silica rock and crystalline calcite (p. 9 of ref. 74) and limestone, silica refuse from ceramic plants, and fluorspar.⁷⁶ Wollastonite melted in an electric-arc furnace has been shown to be experimentally suitable. Tremolite,⁶⁷ hornblende, and soapstone³⁴ also are reported as materials for making rock wool. The well-known woolrock of central Indiana is an impure dolomitic limestone. The average of 20 analyses of this rock showed 31 pct silica-alumina-iron oxide and 32 pct lime and magnesia.⁴⁶

Woolrocks

NATURAL

Natural woolrocks may be divided into two general groups: (1) those comprising a single type of rock, and (2) those made up of a series of thin interbedded dissimilar rock strata that together, but not individually, have the proper CO₂ content. Among the consolidated rocks in the first group are limestones and dolomites high in non-calcareous constituents, such as sand or silt grains, small irregular masses of silica or clay particles, more or less uniformly disseminated through the rock. Rocks of this kind may offer some advantages for making rock wool over rocks composed of larger lithologic units, such as cherty limestone, because of the natural intimate mixture of their constituents.

Other consolidated rocks in the first group are certain types of conglomerates and cherty limestones or dolomites having a matrix comparatively high in carbonates and depending chiefly on the chert for the noncalcareous component. Or the matrix may be impure because of the presence of clay, quartz sand, or disseminated silica, and thus contribute to the noncalcareous content of the material.

In the first group are also calcareous or dolomitic sandstone and shale. Sandstones of this nature usually are well cemented because the calcareous or dolomitic material present occurs at least in part as interstitial filling between sand grains and thus binds the grains together. Calcareous or dolomitic shales contain their carbonates either as relatively large masses such as fossils or nodules, or as small grains intimately mixed with the shale particles. Some shales of the latter type resemble impure limestones and dolomites in appearance, and it is believed that in general they will occur in thicker, more solid strata than shales of the former type.

The unconsolidated rocks in the first group include the unindurated equivalents of the consolidated rocks mentioned above. Some glacial tills belong in this category, as do some calcareous or dolomitic clays, sands, gravels, marls, and other materials.

The second group of natural woolrocks—that is, woolrock consisting of interbedded strata of unlike lithologic character but of such composition that deposits have the chemical composition of woolrock—are commonly interbedded shale and limestone or dolomite, sandstone and limestone or dolomite, or various other combinations of noncalcareous and calcareous rocks. Frequently, in such associations of rock types, none of the types are “pure,” the shales being calcareous or sandy, the sandstones clayey or calcareous, and the limestones and dolomites sandy or clayey. The unconsolidated rocks in this group include the unindurated equivalents of the consolidated rocks.

Some igneous and metamorphic rocks, such as certain peridotites, pyroxenites, talcose, and serpentinous rocks, contain the needed amount of lime and magnesia together with an approximately equal amount of silica and therefore are suitable from the standpoint of composition for making rock wool. However, their iron content is commonly high and special care would be required to ensure a white wool.

Certain minerals, for instance, wollastonite and some of the amphiboles, pyroxenes, talcs and serpentines, are of satisfactory chemical composition for making rock wool.

MIXTURES OR COMPOSITE WOOLROCKS

Mixtures for making rock wool may be compounded of a large number of different earth materials, including sedimentary, igneous, and metamorphic rocks. For example, dolomite and clay, limestone and quartzite, calcite and quartz, or bog lime, clay or sand, in the proper proportions should yield composite woolrocks. In brief, any calcareous rock, consolidated or unconsolidated, containing more than about 65 pct calcium carbonate or calcium and magnesium carbonates, may be combined by suitable processes with consolidated or unconsolidated siliceous or argillaceous rocks in such proportions as to give a composite woolrock.

DELETERIOUS MATERIALS IN WOOLROCKS AND SLAGS

There are no published reports of extensive studies bearing on deleterious materials in woolrocks and slags. Any material that affects adversely the quality of the finished wool must be considered deleterious. It is obvious, therefore, that the type of service to which the wool is put must be considered in this connection.

Stability of a mineral wool toward devitrification is an essential property. This is, of course, a function of the general composition.

Trouble from this source is apt to result from too high ratios of alkaline to acid components. Increasing magnesia content beyond 20 pct shows increasing tendency to favor the formation of crystals. It is conceivable that small amounts of substances such as alkali metal oxides or fluorides might under some conditions impair the stability by acting as mineralizers. The probability of trouble from devitrification increases with the temperature. It is mainly because of this factor that mineral wool is seldom used for insulation where it will be exposed to temperatures much above 550°C. Fryling²⁶ found that most wools show evidence of disintegration after heating for two hours at 800°C.

The presence of sulphur-bearing compounds in the rock or slag may result in formation of compounds such as calcium sulphide in the wool. In the presence of moisture, such compounds will generate bad odors and substances corrosive of metals. Good melting practice and higher cupola temperatures reduce the danger of trouble from this source by eliminating more of the sulphur. Because sulphur usually is present in the fuel if not in the rock or slag, it is probably impossible to avoid it altogether, but in the quantities usually present in commercial wools it is harmless for most applications.

Although the color of mineral wool does not affect its insulating value, color does seem to be important in some sales areas. Fryling²⁶ demonstrated experimentally that although either iron or sulphur may be present in a wool melt in considerable quantity without producing objectionable color, their concomitant presence may produce brown wools. He also suggests that even in such cases longer heating at higher temperatures may produce white wools and that in order to accomplish this result the cupola operation should be controlled to favor reduction of ferrous sulphide to metallic iron by reaction with lime and carbon.⁴⁴

DISTRIBUTION OF DEPOSITS

As rock wool can be made from any woolrock that contains the requisite ingredients in proper proportions, or from artificial combinations yielding mixtures of suitable physical and chemical character, the variety of raw materials of potential use is too great for their distribution to be discussed here. Specific reports have been published regarding the occurrence of natural woolrocks in Indiana,⁴⁶ Illinois,⁴³ Georgia,²⁸ Missouri,⁴⁸ Kansas,⁶¹ Oklahoma,⁸⁴ New Jersey,⁷⁹ Michigan,⁶² Ontario,³⁰ Nova Scotia,⁴⁷ and Great Britain.³³ Reports by various state geological surveys on limestone resources also furnish data.

Production

Available statistics on the production of mineral wool do not differentiate between rock, slag, and glass wool. However, a suggestion as to the comparative amounts of slag wool and rock wool being made is

TABLE 3—*Limestone and Blast-furnace Slag Sold or Used by Producers for Making Mineral Wool*⁵²

Year	Blast-furnace Slag		Limestone	
	Short Tons	Value	Short Tons	Value
1938	45,936	\$41,902	86,400	\$85,378
1939	64,846	60,307	123,720	102,670
1940	63,358 ^a	62,091 ^a	123,700	86,488
1941	155,998	145,114	115,760	93,167
1942	205,966	212,547	119,620	106,985
1943	328,938	330,120	89,590	101,832
1944	307,635	294,481	43,480	45,610
1945	399,932	405,692	39,170	39,575

^a Figures not complete.TABLE 4—*Production of Mineral Wool in the United States*,⁵³ 1942-1944^a

Year	Num- ber of Plants	Num- ber of States	Home Insulation		Industrial Insulation		Total	
			Short tons	Value	Short Tons	Value	Short Tons	Value ^c
1942	52	18	379,142	\$14,916,426	139,430	\$17,890,382	518,572	\$32,806,808
1943	53	19	422,773	18,137,589	128,751	25,533,121	551,524	43,670,710
1944	51	19	434,480	17,578,807	133,816	36,903,989	568,296	54,482,796

^a No detailed production statistics are available subsequent to 1944 but the U. S. Bureau of Mines in a Preprint from Bureau of Mines Minerals Yearbook, 1946, on Minor Nonmetals, page 8, estimates mineral-wool production in 1945 at approximately 720,000 short tons valued at \$70,000,000, with production in 1946 believed to be 20 pct above the 1945 figure.

afforded by the data in Table 3. Probably the tonnage of material used for making rock wool is greater than that shown in the table, as the figures do not include substances added to modify the composition of the limestone or calcareous shales that may be used in making wool. However, it may also be that some of the limestone was blended with slag in manufacture of slag wool. Production of mineral wool in the years 1942 to 1944 is shown in Table 4; later data are not available. Incomplete information for 1945 on the number of mineral-wool plants show 69 plants in 23 states.⁵⁵ In 1946, there were 125 plants in this country.⁵⁰ A breakdown in production in 1944 according to uses is given in Table 5.

Tests and Specifications

Commercial Standard CS 131-46,²⁰ recently promulgated by the National Bureau of Standards, is the first real attempt to set up any sort

TABLE 5—*Production of Mineral Wool in the United States in 1944, by Products*⁵⁴

Product	Home Insulation		Industrial Insulation		Total	
	Short Tons	Value	Short Tons	Value	Short Tons	Value
Loose wool (sold as such)...	59,787	\$1,609,235	5,410	\$188,876	65,197	\$1,798,111
Granulated wool (sold as such).....	308,441	11,344,433	5,178	160,509	313,619	11,504,942
Batts.....	52,007	3,633,878	7,446	1,203,245	59,453	4,837,123
Rolls.....	6,394	372,938	565	30,955	6,959	403,893
Felt.....	4,683	427,393	38,998	5,154,208	43,681	5,581,601
Blocks.....			14,633	1,927,618	14,633	1,927,618
Boards.....			36,728	24,635,485	36,728	24,635,485
Insulating cement.....	1,823	135,861	10,695	825,906	12,518	961,767
Blankets.....	1	148	7,353	1,021,819	7,354	1,021,967
Pipe covering.....			5,240	958,692	5,240	958,692
Other.....	1,344	54,921	1,570	796,676	2,914	851,597
Total.....	434,480	17,578,807	133,816	36,903,989	568,296	54,482,796

of standard tests for the mineral-wool trade. This standard provides uniform methods for testing and reporting the physical and chemical properties of mineral-wool products made of rock, slag, or glass and describes equipment required to produce standard results. Methods of test are included for adhesive strength, compressive strength, corrosion resistance, coverage, density, fire resistance, moisture adsorption, odor emission, shot content, temperature stability, and thermal conductivity. However, to date no generally accepted specifications are known to exist covering mineral wool of various types for specific applications.

Fabrication, Uses and Marketing

SLAG AND ROCK WOOL

The uses of rock and slag wool^{6,12,33} may be grouped into three general categories: heat insulation, sound insulation, and other uses. The principal forms in which the wool is marketed are indicated in Table 5. For home insulation, loose and granulated wool and batts are the principal forms used. Industrial insulation uses the wool mostly as boards, felt, blocks, batts, and blankets.

"Loose wool" is the wool as it comes from the blowing room; it may be processed to remove shot. It is used for insulating new buildings, for filling irregular spaces by hand packing, and for noninsulating purposes such as packing or filter medium for corrosive fluids or air.

"Granulated wool" is made by passing loose wool through machines that break up the long fibers, screen out the shot and roll the wool into small pellets $\frac{1}{2}$ in. or less in diameter. Granulated wool, also known as pelletized or nodulated wool, is the common form blown between the walls of houses for heat insulation.

"Batts" are formed from loose wool by passing it between rollers, which compress the wool to a specified thickness. Thereafter the batts are trimmed to desired sizes. Binders may be used in the process and the batts may be attached to a paper or other backing material. They are used especially for heat insulation in houses and other structures.

"Blocks" are prepared by treating loose wool with binders, commonly of a refractory nature, and compressing the mass, thus forming a rigid but resilient product. Blocks are used for insulating boilers, ovens, and similar equipment, and withstand temperatures up to about 1800°F.

"Blankets" are loose wool, with or without an added binder, commonly contained between a mesh of metal wire and lath or other suitable material. They are from about 1 to 6 in. thick, have a rectangular shape, and are used for insulating furnaces, ovens, flat or moderately curved surfaces in similar types of installations. Felt is generally similar to blankets but usually is without wire or metal lath. Felt is used for insulating cold-storage rooms, fireproofing, and other purposes.

"Boards," made by compressing loose wool with a suitable binder to a specified thickness or by confining it between sheets of other materials, are used for heat and sound insulation.

Cements used for heat insulation of furnaces, boilers, and so forth, are made from granulated or nodulated wool by the addition of a binder such as fire clay or bentonite. For application, the mixture is made plastic by the addition of water.

Pipe covering includes blankets of wool contained between metal fabrics and molded coverings made from a mixture of granulated wool and a suitable binder, which is wetted and shaped and dried in molds to sizes to fit standard pipes.

In addition to the uses described, rock and slag wool are employed for many other special though lesser uses.

GLASS WOOL

The product made by the continuous-filament process is mostly made into glass thread for weaving into fabric and, except for special applications, is not intended for use as heat or sound insulation. The blown product is fabricated into batts, blocks, and other forms and is sold in competition with all forms of rock and slag wool except loose wool and granulated wool.

Prices

Prices on mineral wool in 1944 in carload lots f.o.b. plants were \$37.50 for loose wool and \$53 for granulated wool. These prices were under government control.⁵⁴ Prices on other types of products in the same year are suggested by the data in Table 5.

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CHAPTER 22

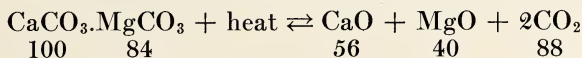
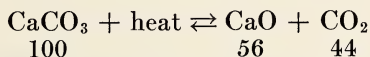
LIME

BY NATHAN C. ROCKWOOD*

LIME is a very general term applied to products of limestone, in popular treatises often incorrectly, including ground or pulverized limestone used in agriculture. When used without qualifying adjective, the term usually means burned or calcined limestone, or quicklime, or calcia.

The corresponding calcined product of magnesite is magnesia. If the calcined rock is relatively pure calcium carbonate, the resulting lime is a "high-calcium" lime; if the rock is dolomite, or a combination of calcium and magnesium carbonates, the lime is a "dolomitic" or a "high-magnesium" lime. There are various grades in between, depending on the percentage of magnesium carbonate and other ingredients in the raw rock. For some industrial purposes only high-calcium limes are suitable; in other processing—as, for example, neutralizing acid wastes—the relative percentages of magnesium and calcium carbonates in the raw material are not important.

Limestone is burned (roasted or calcined) in furnaces known as lime kilns by direct exposure to the hot gases and flames. When heated to incandescence, the carbon dioxide content of the rock is expelled, leaving calcium and magnesium oxides, according to the formula usually written:

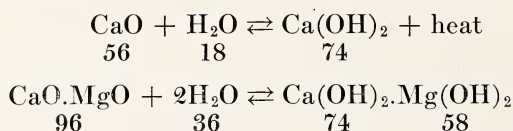


This thermal reaction is reversible, which requires that the lime be withdrawn from the "calcining zone" of the kiln about as fast as made. Pure calcium carbonate would lose 44 pct of its weight in the calcining process; dolomite, 48 pct.

Generally, the lime will retain the approximate size and shape of the piece of rock from which it is made but some few limestones tend to break down into granules or dust. Hence lime (quicklime) comes from the kilns in lumps or granules and normally is packed in water-tight containers in these forms, or is pulverized after calcination.

* Editorial Consultant, *Rock Products*, Chicago, Illinois.

Lime has great affinity for moisture and carbon dioxide; therefore it is a perishable commodity. When combination occurs slowly, due to exposure to the atmosphere, the resulting product is "air-slaked." Since the reaction with water involves the evolution of considerable heat, lime cannot safely be shipped or stored in bulk unless amply protected. Fires in railway cars and storehouses have been caused by leaking rain water. Consequently, much of the commercial lime is prepared in the form of a dry hydrate powder, which is a more stable and readily handled commodity. Since nearly all industrial uses of lime involve association with water, hydrated lime (calcium hydroxide) is interchangeable with quicklime for practically all purposes. The hydrating is done mechanically with just the right amount of water, according to the chemical reaction:



This reaction also is reversible and one method of making a practically pure calcium oxide is to reheat a purified hydrate to expel the water of crystallization. The heat of hydration is utilized in some types of fireless cookers or small food or beverage heaters.

PROPERTIES

Lime owes its industrial value primarily to the fact that it is the commonest and cheapest of alkali chemicals; therefore it is widely used as a base, causticizer, and neutralizer. For construction purposes, lime is the cheapest mortar and plaster material, primarily because of its physical properties for making plastic mixtures, in relatively lean proportions, that harden on exposure to moist air. In agriculture, its value is threefold: (1) it neutralizes acid soils; (2) it improves the physical condition of heavy soils; (3) it supplies calcium, magnesium, and some of the rarer mineral food requirements of growing plants and animals.

The value of lime for most purposes is dependent on its content of available calcium oxide, or the sum of its available calcium and magnesium oxides, for the particular process involved. A few limestones contain more than 99 pct pure carbonates but the majority of limestones are seldom more than 97 pct pure. The chief impurities are silica, alumina, and iron, which react with the calcium oxide in the kilns and tie up a part of the lime in mineral forms unavailable for chemical uses but are not detrimental to its use in construction. Where the percentages of silica and alumina are considerable, and the silica is present as a silicate rather than quartz, the product made is hydraulic

lime, which may be preferred for mortar, or even for plaster, since it has considerable tensile and compressive strength when hardened.

Calcining impure limestones by reducing the weight increases the percentage of impurities in the finished product, of course, as well as reduces the available calcium and magnesium oxides through chemical combination with the impurities. When the dry hydrate is milled in a pulverizer equipped with an air-separation device, a large percentage of the impurities is rejected, so that in hydrated lime a purer oxide equivalent content is possible. However, 24 pct of hydrated lime is water of crystallization, so that for purposes that do not require too pure a product, quicklime is the more concentrated or economical form.

Other impurities in lime, derived both from the impurities in the limestone and from the lack of thoroughness of calcination and the kind of fuel used in the kiln, are sulphur, phosphorus, arsenic, manganese, uncalcined carbonate, and traces of almost any of the rarer minerals. Some common impurities are highly objectionable for certain uses of lime; iron, for example, because of its staining effect and chemical activity. Even traces of arsenic and fluorine in lime used in food processing are objectionable.

Lime (quicklime) is usually white or cream colored but may be buff or gray, depending on the nature of the impurities rather than on their amount. If it has been calcined without reaching excessively high temperatures or too long retention in the calcining zone, there is little shrinkage in the size compared with that of the rock. The exit of carbon dioxide has left open pores, which comprise about 55 pct of the volume of the fragment. The structure usually is called amorphous but actually is cryptocrystalline, since it has a definite X-ray pattern. Long calcination periods and/or temperatures in excess of about 2500°F cause some shrinkage, with resultant loss of pore space; thus producing lime that hydrates more slowly, or is less "chemically active."

A properly calcined high-calcium lime is a "hot" lime—it hydrates rapidly with the evolution of much heat. A "hard-burned" lime, or one with considerable impurities, hydrates more slowly, but given proper treatment and sufficient time, recent tests seem to show that about the same end points in regard to the properties of the hydrates are achieved. A dolomitic or magnesium lime hydrates more slowly because at first only the calcium oxide is hydrated. By soaking for a considerable period of time, or by the use of a steam-pressure hydrator, or other special means, the magnesium oxide may be converted to a hydrate.

While one of the commonest and most ancient manufactured products, limes from different sources have peculiarities still positively unaccounted for scientifically. Consequently, there is no overall specifica-

tion for lime used in various industrial processing, and no attempt has ever been made to standardize the product in the sense that portland cement has been standardized. Processes often have been adapted to the use of a lime from a single source and under ordinary conditions processors may be reluctant to make changes; hence, there are a multitude of specifications, or purchase requirements, which sometimes only the user knows the reasons for.

LIMESTONE—ORIGIN AND MODE OF OCCURRENCE

Limestone (or lime rock) is the source of raw material for most of the lime manufactured but calcium carbonate or hydrate from any source may be used in a properly selected type of kiln. Crushed and washed oyster shells are used to a considerable extent; also calcium carbonate and hydrate wastes from the paper and other industries. Such waste, in the form of sludge or slurry, is calcined in rotary kilns, usually with the addition of limestone.

Limestones are sedimentary rocks, which occur in practically inexhaustible quantity in nearly all parts of the world and in an infinite number of varieties. The calcium and magnesium carbonate minerals of which limestones are largely composed are calcite, aragonite, dolomite and magnesite. According to F. W. Clarke (*The Data of Geochemistry*, U. S. Geol. Survey, *Bull.* 695, 4th Ed., 1920), these four minerals have the following characteristics:

Calcite—Rhombohedral. Composition, CaCO_3 . Molecular weight, 100.1. Specific gravity, 2.72. Molecular volume, 36.8. Hardness, 3. Normally, colorless, but often variously colored by impurities.

Aragonite—Orthorhombic. Composition, CaCO_3 like calcite. Specific gravity, 2.94. Molecular volume, 34. Hardness, 3.5 to 4. Color, white, but often tinted by impurities.

Dolomite—Rhombohedral. Composition, CaMgC_2O_6 . Molecular weight, 184.5. Specific gravity, 2.83. Molecular volume, 65.2. Hardness, 3.5 to 4. Normally colorless but often tinted pink or brown.

Magnesite—Rhombohedral. Composition, MgCO_3 . Molecular weight, 84.4. Specific gravity, 3.0. Molecular volume, 28.1. Hardness, 3.5 to 4.5. Color, white or brown.

Most high-calcium limestones are composed principally of calcite; aragonite is a less stable form of calcium carbonate and apparently changes by exposure and with time to calcite, but there are limestone deposits in dry sections near the Pacific Coast of the United States that are said to contain a considerable percentage of aragonite. Some geologists believe dolomite exists in two forms: (1) the double carbonate of calcium and magnesium; (2) a mechanical mixture of calcite and magnesite.

According to Clarke, all the four carbonates listed above occur in

igneous rocks, and calcite is sometimes found to be of apparent primary origin. When heated under ordinary conditions, calcite is decomposed into CaO and CO_2 , but under very great pressures it can be melted without decomposition; thus, it is not impossible that there are calcite deposits that may have been formed during the solidification of a magma at great depth.

The commercially important deposits of limestone generally consist of marine sediments—shells and skeletons of plants and animals ground to fragments of various sizes and consolidated by pressure and precipitation of calcite or calcium silicate binders. Such deposits have been formed in both fresh water and inland seas, and are being formed today. Clarke writes that some limestone, the variety known as calcareous tufa or travertine, is a chemical precipitate, but in its larger masses, the rock is generally of organic origin; that is, remains of both plant and animal life. As in other sedimentary deposits, silica, clay and organic materials were often deposited with the calcium and magnesium carbonates. Thus there are siliceous, argillaceous, glauconitic, ferruginous, phosphatic, and bituminous limestones.

Granular composition of limestones varies greatly from inclusions of whole casts of fossil plants and animals to “amorphous” material deposited probably as slime or dust. The fossils are useful in identifying the geologic age and general character of the deposit but the same geologic strata may vary greatly in other characteristics in different localities, because of special conditions at the time and place of deposition. The granular composition of the stone is important in deciding on the calcination method, for fine-grained and coarse-grained, compact and porous, stones often show different characteristics at calcining temperatures, so that it is practically impossible to burn some stones in any but rotary kilns.

Hand-picking limestone, identified by certain fossils, has made it possible for a few lime manufacturers to make a half dozen varieties of lime for special purposes, such as lapping lime, for lapping gemstones; lime for “lime water”; lime for neutralizing rancid butter. The differences from other limes are more in the texture of the stone and the resulting lime than in the chemical composition, but each requires certain precautions in the calcining process.

The origin of dolomite and dolomitic limestones is not known positively but it is generally assumed that they were deposits of calcium carbonate in waters subsequently high in magnesium salts, and that the magnesium has replaced the calcium by infiltration and chemical reaction. Calcium carbonate, or calcite, is only slightly soluble in water at ordinary temperatures and pressures but its solubility increases with lower temperature and high pressures. Magnesium carbonate is slightly more soluble. This difference has been made use of in

patented methods of leaching dolomite with water or mild acid solutions to remove the magnesium carbonate and leave the calcium carbonate.

In general, workable deposits of high-calcium limestone are more valuable than similar deposits of dolomite or magnesium limestones, for the marketing possibilities of high-calcium lime are greater. Magnesium carbonate, where it exists in amounts greater than 3 pct in the rock, usually prohibits use of that limestone for manufacture of portland cement and for use in many chemical industries. On the other hand, magnesium limestones and limes are often preferred for agricultural use because the magnesium oxide and carbonate have relatively greater neutralizing value for acid soils than the corresponding calcium minerals, and also supply the element magnesium, which is a very important plant food and fertilizer, particularly for tobacco and some fruit trees. Magnesium limes are generally preferred for white-coat finishing plaster, since they often make more plastic putties.

DISTRIBUTION OF DEPOSITS

Limestone deposits of commercial importance have been found in every state in the United States except Delaware and New Hampshire. The United States Geological Survey has published (1914) a map showing the principal limestone deposits east of the Rocky Mountains, differentiating between high-calcium and dolomitic areas. A similar map, or an extension of this map, west of the Rocky Mountain states, has never been prepared, but maps have been made showing the locations of all lime plants existing in 1913, which includes the far western states (see Minerals Yearbook, 1941, chapter on lime, by Oliver Bowles and F. D. Gradijan).

Analyses of typical limestones used for the manufacture of lime are shown in Table 1.

New England States—The important limestone deposits in Maine are near the coast at Rockland and Thomaston. They are high-calcium rock occurring in vertical or steeply dipping beds and are worked by open quarries, some of considerable depth. In Vermont, Massachusetts, and Connecticut, the deposits are mostly highly crystalline, both high-calcium and dolomite, and are quarried for marble as well as for lime. In Rhode Island, a relatively small deposit of low-magnesium limestone occurs, from which the first "stone lime" used in Colonial New England was manufactured. Prior to that, oyster shells were burned in heaps.

New York, New Jersey, and Pennsylvania—These three states, particularly New York and Pennsylvania, have many important deposits of both high-calcium and magnesium limestones, which are the sources of raw material for numerous lime and portland-cement plants. Many

TABLE 1—*Analyses of Limestones^a*

Company and Location	Designation of Stone	Composition, Pct						
		Silica (SiO ₂)	Alu- mina (Al ₂ O ₃)	Iron (Fe ₂ O ₃)	Calcium Carbon- ate (CaCO ₃)	Magne- sium Carbon- ate (MgCO ₃)	Mois- ture	Total
Rockland and Rockport Lime Co., Rockland, Me.	{ Soft Rockport	1.29 2.41	0.15 0.22	0.35 0.40	95.91 85.18	2.27 11.72		99.97 99.93
Farnam-Cheshire Lime Co., Cheshire, Mass.	^b	0.44	0.08	0.20	98.05	1.30		100.07
Connecticut Lime Co., Canaan, Conn.	^b	0.34	0.19	0.28	58.20	41.16		100.17
New Jersey Lime Co., Hamburg, N. J.	{ McAfee Hamburg	0.85 1.21	0.06 0.41	0.20 0.45	96.70 95.70	2.04 2.25		99.85 100.02
Chas. Warner Co., Cedar Hollow, Pa.	{ South quarry: West End East End North quarry Whiteland	0.81 0.91 2.27 0.94	0.56 0.09 0.51 0.15	0.47 0.30 0.40 0.45	54.68 63.02 53.16 54.09	43.66 35.78 43.89 44.58		100.17 100.10 100.23 100.21
Palmer Lime Co., York, Pa.	{ White Blue Calico	0.53 0.14 0.27	0.04 0.02 0.07	0.05 0.10 0.30	99.21 98.73 86.43	0.74 1.01 12.98		100.57 100.00 100.05
American Lime and Stone Co., Bellefonte, Pa.	Quarry No. 13	1.41	0.25	0.40	96.36	1.55		99.97
Thomasville Stone and Lime Co., Thomasville, Pa.	^b	0.15	0.10	0.15	99.02	0.57		99.99
Riverton Lime Co., Riverton, Va.	{ Slaty Oily	0.42 0.36	0.07 0.07	0.32 0.22	97.20 96.07	2.02 3.26		100.03 99.98
E. Dillon's Sons, Indian Rock, Va.	^b	0.46	0.06	0.20	89.20	10.14		100.06
Tennessee Marble Lime Co., Knoxville, Tenn.	{ Upper quarry Lower quarry Fertilizer Main quarry Other quarry Luttrell	0.28 0.80 1.05 0.16 0.23 0.65	0.16 0.10 0.40 0.13 0.08 0.05	0.20 0.35 0.55 0.06 0.20 0.30	98.50 97.05 96.21 98.93 98.25 84.50	0.78 1.72 1.76 0.76 1.26 14.53		99.92 100.02 99.97 100.04 100.02 100.03
Lagarde Lime and Stone Co., Lagarde, Ala.	^b	1.64	0.33	0.31	94.39	3.42		100.09
Ash Grove Lime and Cement Co., Ash Grove, Mo.	^b	0.10		0.05	99.05	0.88		100.08
Glencoe Lime and Cement Co., Glencoe, Mo.	{ Gray Blue Brown White ^c	0.32 0.21 0.26 1.35	0.13 0.06 0.02 0.53	0.30 0.15 0.20 0.40	98.29 98.89 98.84 94.89	1.05 0.67 0.65 3.05		100.09 99.98 99.97 100.22
Marblehead Lime Co., Marblehead, Ill.	^b	0.21	0.04	0.10	98.45	1.28		100.08
Sheboygan Lime Works, Sheboygan, Wis.	^b	0.55	0.24	0.40	55.09	43.91		100.19
Union Lime Co., High Cliff, Wis.	^b	1.12 1.92	0.06 0.03	0.40 0.30	54.82 54.04	43.79 43.81		100.19 100.10
White Marble Lime Co., Manistique, Mich.	{ Manistique ^c Blaney Marble Indian	1.23 0.56 1.04	0.19 0.05 0.05	0.50 0.20 0.25	94.38 55.00 54.25	3.74 44.31 44.52		100.04 100.12 100.51
Woodville White Lime Co., Woodville, Ohio.	^b	0.34	0.02	0.15	56.79	42.92		100.22
Louisville Cement Co., Milltown, Ind.	^b	0.46	0.09	0.05	99.20	0.25	0.07	100.12
Glencoe Lime and Cement Co., Glen Park, Mo.	^b	0.24	0.14	0.02	98.30	tr	0.15	98.85
Peerless White Lime Co., Ste. Genevieve, Mo.	{ White Gray Baby milk ^b Milk ^c Vienna Horologic Lump	0.20 1.60 0.78 0.38 0.14 0.16 0.80	0.01 0.02 0.13 0.19 0.21 0.18 0.11	0.03 0.08 0.05 0.07 0.05 0.04 0.09	99.40 95.00 54.80 54.50 54.80 55.40 55.00	0.40 3.30 45.00 45.00 45.00 45.30 44.75	0.02 0.03 0.16 0.04 0.05 0.05 0.05	100.06 100.03 100.92 100.18 100.25 101.08 100.80
Ohio Hydrate and Supply Co., Woodville, Ohio.	^b	0.34	0.02	0.15	56.79	42.92		100.22
Kelley Island Lime and Transport Co., Marblehead, Ohio.	^b	1.75	0.36	0.11	87.70	10.10		100.02

^a From Burchard and Emley¹⁸ and Bureau of Standards.⁵⁰^b Average of stone burned for lime.^c Not burned for lime.

of these deposits, especially in the Appalachian Mountain Range sections of central Pennsylvania, have been folded and upended, so that underground mining is sometimes necessary; and where open-pit quarrying is employed, stripping of overburden frequently is a major problem.

Maryland, Virginia, West Virginia, North Carolina—The limestone deposits in these four states are chiefly high-calcium and are similar to those in Pennsylvania in that they occur in the Appalachian Mountain Range, in the western parts of the states, and are frequently folded and upended. Some soft limestones and marls occur in the coastal plain but are not of much importance. Some of the mountain deposits are metamorphosed or crystalline limestone (marble). The deposits in the three northern states are important sources of both lime and limestone for chemical and metallurgical purposes.

Tennessee, Mississippi, Alabama, Georgia, and Florida—Tennessee deposits occur in all varieties from marble to argillaceous and phosphatic limestone. Manufacture of lime and portland cement are important industries. Most of the deposits worked are of high-calcium stone. In Mississippi are two broad belts of high-calcium limestone deposits, one in the northeast corner of the state and the other extending west to east in the south central part. Both extend across the state of Alabama and the southernmost one extends into southwest Georgia. Deposits in northern Alabama and northeast Georgia are extensions of the same kind of limestone that occurs in the northern part of the Appalachian Mountain Range. The Alabama and Georgia deposits are important sources of raw material for the manufacture of lime and portland cement and are sources of metallurgical limestone. Limestone in the form of coral and shell rock is widely distributed in the state of Florida and is used for lime and portland cement manufacture. These deposits are at or near the surface, are generally soft rock, and are easily quarried.

Ohio, Indiana, Illinois, and Kentucky—The western half of Ohio and nearly all the state of Indiana is underlain with almost continuous deposits of limestone, much of it of Niagara dolomite formation. The same formation extends around Lake Michigan into northern Illinois and eastern Wisconsin. The most important deposits in Indiana are in a belt of high-calcium rock about 20 miles wide, extending northward through the central part of the state and including the famous Indiana oölitic limestone in the Bedford and Bloomington districts—widely used for dimension stone because of its pleasing appearance and easy workability. Waste from the dimension-stone quarries, a high-calcium rock, is used to make lime. In Illinois, the present lime industry, which utilizes native high-calcium stone, is located along the Mississippi River at Quincy and Alton. In the Chicago metropolitan area,

high-calcium limestone brought from Michigan quarries is used, and local dolomite is used mainly for the manufacture of sintered dolomite refractories. Kentucky has many outcrops of the same limestone formations that exist in Ohio and Indiana but the limestone there is used largely for aggregate and agricultural limestone.

Wisconsin and Michigan—The southern peninsula of Michigan at some geological period enclosed a well-defined inland-sea basin, and limestone, gypsum, and salt deposits are widely distributed, although outcrops of limestone are scattered, the most important ones commercially occurring in the north along the shores of Lakes Huron and Michigan. Because of their accessibility to water transportation, quarries here are important sources of limestone for lime, cement, and metallurgical industries. Dolomite occurs in Wisconsin in a fairly broad belt in the eastern part of the state, bordering Lake Michigan. No deposits of high-calcium limestone are known in this state.

Minnesota, Iowa, Missouri, Oklahoma, Arkansas, and Louisiana—Extensive deposits of dolomite occur in the southeast corner of Minnesota. South of these deposits is a broad belt of high-calcium limestone, which extends through central and southeast Iowa to the Mississippi River. There are also extensive deposits of high-calcium limestone in western Iowa and along the Missouri River. Practically the whole state of Missouri is underlain by limestone, both high-calcium and magnesium, and the southern limits of these deposits extend into the northeast corner of Oklahoma and northern Arkansas, where several lime plants are established. Louisiana contains only one or two known deposits of commercial importance; one near Alexandria has been quarried for the manufacture of lime. Oyster shells are used for making lime in Louisiana.

Texas—Limestone occurs in many places in Texas, usually in deposits of high-calcium stone of no great purity. At New Braunsfels, near San Antonio, is an important lime industry. There are also deposits near Austin and El Paso from which lime is made, and dredged oyster shells are used at Houston.

North and South Dakota, Nebraska, and Kansas—Limestone deposits probably exist in many places in these plains states but, because of lack of markets, no particular effort has been made to find or develop them. The soils of this region are still sufficiently alkaline to require little if any lime but finely ground limestone is produced in Kansas as an addition to animal fodder.

Rocky Mountain States—The Rocky Mountain tier of states contains many unexplored deposits of limestone and dolomite, but except for the metallurgical and building markets, which are not large in this section, there has been little effort to find and explore such deposits. Utah, Colorado, and Nevada have important lime industries and lime-

stone is quarried in some of these and the other Mountain states chiefly for manufacture of cement and for the beet-sugar industry.

Pacific Coast States—Numerous outcrops of limestone occur along and near the entire Pacific Coast of the United States and supply raw material for both lime and cement manufacture. These deposits are of increasing commercial importance because of the growth of industry in these states and the increasing use of lime in West Coast agriculture.

Canada and Mexico—There are extensive deposits of limestone in Canada but those of commercial importance at the present time are confined chiefly to the more thickly populated sections of Quebec, Ontario, Manitoba, and British Columbia. Mexico also has many deposits of limestone similar to those of our Mountain states. These are of increasing importance for the manufacture of lime for insecticides and other agricultural uses. Lime is an ancient building material in Mexico but the manufacture of purer products for industrial uses is new.

World in General—Limestones are fairly well distributed throughout the world for they were formed somewhere, apparently, during all known geological periods from Cambrian down. Except in industrialized countries, no great effort has been made to explore the limestone resources of the world, but evidently they are ample for all time. It is interesting and significant that colonists in all parts of the world have sought limestones for building and metallurgical purposes with no less zeal than they have searched for precious metals.

POLITICAL AND COMMERCIAL CONTROL

With such a cheap and common industrial mineral as limestone so widely distributed throughout the world, lime is seldom a commodity of importance in international trade. Special kinds of lime—for instance, Vienna lime, used as an abrasive for polishing glass lenses, surgical instruments, and so forth, and lapping lime, a similar product—enter international trade on a very small scale. In general, however, most localities are able to supply their own requirements, either from limestone or from oyster shells.

In the United States, a small amount of the lime made is exported to outlying islands, to Mexico, Central America, and South America; in some instances more from want of cheap fuel and know-how in the importing country than from lack of limestone or other raw material. In 1945, some 24,276 short tons, valued at \$268,875, was exported, most of it to Canada (8379 tons), Honduras (6017 tons), Mexico (4587 tons), and Panama (3716 tons). The lime shipped to Canada was chiefly for chemical uses and that to Central America both for construction and for treating a banana-plant disease, in which lime has proved effective. Exports have been as high as 46,500 tons (1941).

Very little lime is imported into the United States (20,785 short tons, valued at \$179,177, in 1945) and practically all of that came from British Columbia into the state of Washington. The import duty is 50¢ per ton for quicklime and 60¢ per ton for hydrated lime, as established by the Geneva convention. At this writing (September 1947) the tariff on lime and limestone was scheduled for consideration in a new reciprocal trade agreement. Except in British Columbia, Canada has no exportable surplus of high-calcium lime for use of industry, but large deposits of dolomite exist in the Georgian Bay area of Ontario, which could be shipped by water on the Great Lakes.

PRODUCTION AND CONSUMPTION

Production and consumption of lime in the United States have fluctuated between wide limits in recent years. During the building boom years of the 1920s it reached more than 4,500,000 tons a year; in the depression year of 1932, it sank to less than 2,000,000 tons. The loss was caused by shrinkage of all markets and that in the building materials market has been more or less permanent, owing to the growing use of gypsum plaster and wallboard and to the use of masonry mortar cements of various kinds, generally with natural or portland cement as the basic ingredient. Because of the activity of the National Lime Association in research and promotion, lime has recovered some of its former markets as a masonry material in combination with portland cement, usually on a 1:1:6 basis (1 cu ft of cement, 1 cu ft of hydrated lime or lime putty, 6 cu ft of sand). Such mortar is claimed to have ample tensile and compressive strengths, to have better plastic and water-retentive properties, better adherence to masonry units, less shrinkage upon hardening, and more nearly to provide waterproof walls than straight portland-cement mortars.

With the rapid growth of the industrial, chemical, and plastic industries in the United States following the business depression of the 1930s, the production and consumption of lime increased rapidly; in 1940, the total was 4,886,929 tons valued at \$33,956,385; in 1943, the top year according to the annual statistics of the U. S. Bureau of Mines, 6,596,615 tons valued at \$49,064,328; in 1945, the latest available figures, 5,920,579 tons valued at \$45,918,468, or an average net of \$7.76 per ton. These figures are not strictly comparable with early estimates of production and consumption because they include lime and lime products such as precipitated calcium carbonate (very small tonnage) and similar special products, and also include lime used by the producers and not sold as lime (alkali, paper, beet sugar, calcium carbide manufacturers, and others), the so-called "captive tonnage." In 1945, this captive tonnage was estimated at 368,572 tons valued at \$2,216,373, or about 6.2 pct of the total tonnage; 4.8 pct of the total value. Of the

1945 total, 1,355,028 tons valued at \$11,422,254 (\$8.43 per ton) was shipped as hydrated lime.

No one has ever attempted to tabulate *all* the multitudinous uses of lime but a fair idea is contained in Table 2.

Lime, being a perishable commodity, is not carried in stock for any considerable period, therefore the statistics of annual production are to all practical purposes also the statistics of consumption.

PROSPECTING AND EXPLORATION

The extent to which prospecting and exploration of limestone deposits should be carried out depends upon several factors: (1) the size of the expected operation, (2) the extent and character of the exposed ledge, (3) the kind of lime product to be made, (4) the kind of mining operation to be employed, and others. Many small limestone quarries have been opened and worked for years. Mere sampling of the exposed face at various places may be all that is required for these or a moderate-sized operation, and hundreds of small lime plants with two or more shaft kilns have been established on such data. On the other hand, the number of these small operations in the lime industry has been steadily diminishing for many years, and the lime industry in the United States in 1945 had become one of only 189 producers, compared with more than twice that number in the 1920s and about five times that number in the early years of the present century. Of the 189 active producers, 73, producing annually from 25,000 to 100,000 tons or more each, accounted for 87 pct of the entire tonnage. It follows, therefore, that a modern lime plant, requiring a capital investment of probably not less than half a million dollars, justifies a scientific determination of the quality and extent of the limestone deposit.

Thorough core-drilling is the usual practice, with adequate study of both the chemical and physical characteristics of the rock cores, followed by trial burns of rock samples in pilot kilns or in the kiln of some lime plant. It is common practice to ship rock by the carload to some established kiln for a trial burn under actual operating conditions. Most limestone deposits vary considerably at different depths and these differences must be taken into account in determining how the rock is to be mined, and whether or not some method of selection is to be required. Not only changing chemical composition but various physical characteristics may be encountered that will affect the selection of quarrying or mining methods and the type of crusher to be used. Slabby fragmentation is to be avoided in all sizes.

The rapid decrease in the number of lime-plant operations and the increase in size of the survivors have been due not only to the stronger commercial position of the large producers but to the fact that they have introduced scientific methods of exploring and developing their

TABLE 2—*Lime (Quick and Hydrated) Sold by Producers in the United States, 1945–1946, by Uses^a*

Use	1945			1946		
	Short Tons	Value		Short Tons	Value	
		Total	Average		Total	Average
Agricultural.....	373,410	\$2,906,844	\$7.78	384,658	\$3,151,613	\$8.19
Building:						
Finishing lime.....	229,034	2,131,458	9.31	347,237	3,535,208	10.18
Mason's lime.....	241,802	2,111,177	8.73	389,003	3,996,480	10.27
Prepared masonry mortars.....	27,693	193,274	6.98	45,631	352,950	7.73
Unspecified.....	51,018	473,455	9.28	63,733	742,060	11.64
	549,547	4,909,364	8.93	845,604	8,626,698	10.20
Chemical and industrial:						
Alkalies (ammonium, potassium, and sodium compounds).....	b	b	b	2,572	21,528	8.37
Asphalts and other bitumens.....						
Bleach, liquid and powder ^c	24,712	192,041	7.77	13,872	124,239	8.96
Brick, sand-lime and slag.....	12,641	108,974	8.62	18,667	164,049	8.79
Brick, silica (refractory).....	15,332	139,105	9.07	14,665	133,153	9.08
Calcium carbide and cyanamid.....	364,944	2,534,625	6.95	377,694	2,806,965	7.43
Chromates and bichromates.....	36,252	239,812	6.62	28,378	201,700	7.11
Coke and gas (gas purification and plant byproducts).....	31,173	221,576	7.11	25,675	198,976	7.75
Explosives.....	15,531	124,933	8.04	1,579	14,399	9.12
Food products:						
Creameries and dairies.....	7,298	69,792	9.56	3,232	37,546	11.62
Gelatin.....	5,027	38,091	7.58	5,270	44,186	8.38
Stock feed.....	10,798	109,718	10.16	8,503	114,564	13.47
Other ^d	4,584	43,774	9.55	9,333	90,992	9.75
Glassworks.....	220,853	1,631,019	7.39	248,693	1,949,215	7.84
Glue.....	9,148	70,114	7.66	8,179	67,786	8.29
Grease, lubricating.....	2,068	15,282	7.39	2,722	22,346	8.21
Insecticides, fungicides, and disinfectants.....	82,507	713,465	8.65	96,457	888,114	9.21
Magnesia (85 pct).....	23,647	210,544	8.90	26,376	246,495	9.35
Medicines and drugs.....	7,897	53,560	6.78	10,517	77,345	7.35
Metallurgy:						
Nonferrous smelter flux.....	7,442	59,695	8.02	9,560	76,030	7.95
Steel (open-hearth and electric furnace flux).....	1,064,005	7,136,870	6.71	874,243	6,390,713	7.31
Ore concentration ^e	342,742	2,316,172	6.76	205,541	1,585,993	7.72
Wire drawing.....	16,645	147,508	8.86	13,527	125,111	9.25
Other ^f	11,868	94,879	7.99	41,073	348,467	8.48
Paints.....	18,950	136,215	7.19	25,598	239,113	9.34
Paper mills ^g	510,832	3,740,694	7.32	565,839	4,489,033	7.93
Petroleum refining.....	53,176	448,091	8.43	48,387	446,532	9.23
Rubber manufacture.....	7,170	51,133	7.13	3,193	26,516	8.30
Salt refining.....	1,884	13,103	6.95	4,384	32,067	7.31
Sewage and trade-wastes treatment.....	71,496	561,649	7.86	65,514	503,037	7.69
Soap and fat.....	5,221	33,246	6.37	2,897	20,572	7.10
Sugar refining.....	24,584	279,843	11.38	26,887	345,687	12.86
Tanneries.....	81,213	613,493	7.55	80,182	649,290	8.10
Varnish.....	364	3,460	9.51	502	3,766	12.47
Water purification.....	402,158	3,034,810	7.55	431,772	3,565,522	8.26
Wood distillation.....	1,265	11,624	9.19	3,830	29,660	7.74
Undistributed ^h	25,032	255,843	9.42	73,614	704,735	9.57
Unspecified.....	289,829	2,053,796	7.09	305,728	2,307,039	7.55
	3,810,288	27,488,549	7.21	3,684,455	29,152,499	7.91
Refractory lime (dead-burned dolomite).....	1,187,334	10,613,711	8.94	1,077,983	10,101,707	9.37
Total lime ⁱ	5,920,579	45,918,468	7.76	5,992,700	51,032,517	8.52
Hydrated lime included in above distribution.....	1,355,028	11,422,254	8.43	1,648,369	15,083,399	9.15

^a Minerals Yearbook, 1946. U. S. Bur. Mines.^b Included under Undistributed.^c Excludes bleach used in paper mills.^d Includes chocolate, cocoa, fruit juices, phosphate baking powders, and unspecified food products.^e Includes flotation, cyanidation, bauxite purification, and magnesium manufacture.^f Includes mold coating and unspecified.^g Includes bleach used in paper mills.^h Includes acid neutralization, alcohol, calcium carbonate (precipitated), cement manufacture, polishing compounds, retarder, sulphur, textiles, and wool pullers; in addition, alkalies in 1945 and asphalts and other bitumens in 1946.ⁱ Includes lime¹ used by producers (captive tonnage) as follows—1945: 368,572 tons, \$2,216,373; 1946: 328,837 tons, \$2,216, 551.

limestone resources, to make superior and uniform products. Improvements in manufacturing to reduce costs have played a part also, of course, but no more important a one than scientific use of the raw materials. Limestone that is not suitable for making lime, either because of quality or size of particle, is commonly used for mineral aggregates, mineral fillers, and agricultural limestone. Impure limestones (containing silica, alumina, and iron) are used by some lime manufacturers to manufacture rock wool.

Since core-drilling is common to all mineral industries, it is not considered necessary here to explain in detail the methods employed in exploring a limestone deposit. Such a survey is simpler than locating the vein of an ore body because often all that is necessary is to determine the depth of overburden and the boundaries of the deposit and to find out whether or not it is of fairly constant composition.

The value to be placed on a limestone deposit for its use in the manufacture of lime will depend on various factors: (1) its location and accessibility; (2) the availability of fuel at reasonable cost; (3) its purity; (4) its extent; (5) its value for other purposes. Most deposits have been acquired in fee simple at farmland or wood-lot value. Where stone is taken from leased property, the royalty has varied from 5¢ to 25¢ per cubic yard of limestone produced. Probably the commonest royalty for good limestone for any purpose is 10¢ per cubic yard of rock quarried.

MINING AND QUARRYING METHODS

By far the largest tonnage of limestone used for lime manufacture is obtained by open quarrying, because in many important lime-producing areas the limestone deposits are in horizontal or only slightly dipping strata, usually accessible without excessive stripping operations. Open-pit methods have been widely adopted because both producers and labor available are more familiar with quarrying than with underground mining, and because in most large operations considerable volumes of limestone are produced for other products than lime.

Where the operation is exclusively for the production of lime in vertical or shaft kilns, the quarrying is very simple. The object is to avoid production of fines, and drilling and blasting are designed accordingly. The use of compressed-air drills, both the hand-hammer type and mounted wagon drills, is regular practice. The rock is often hand-picked and loaded into small industrial railway cars or into skips, which are picked up by specially designed motor trucks or by cableways. The cars or skips are then conveyed direct to the tops of the kilns and dumped. Such an operation requires a minimum of mechanical equipment and in isolated localities and for relatively small production is still normal, good practice.

The introduction of a power shovel in the quarry may also require

the use of well or churn drills, the installation of a crusher and scalping screen, and a more elaborate method of feeding the kilns. Hand-operating methods probably are seldom justified when annual production exceeds 25,000 tons of lime, which would require quarrying approximately 50,000 tons of rock, or 200 tons per day in a 250-day operating season. When hand sorting is necessary for larger tonnages, it is more economical to sort the lime than the rock. In large quarries, the methods of quarrying are no different from those employed for the manufacture of portland cement or the production of crushed stone.

Underground mining of limestone for the manufacture of lime has been increasing slowly for a number of years, for several reasons. Producers have found that where room-and-pillar methods are employed, with rooms of sufficient size for the operation of standard power shovels and an industrial railway or motor trucks, costs are practically the same as in open-pit quarrying. The greater costs for drilling and blasting are offset by year-round operation in all weathers and a cleaner and more uniform quality of rock. The moisture in newly mined rock appears to be an aid to calcination. Most such mines are entered from former quarry-floor levels but in a few places the deposit is accessible only by means of shafts, which must be equipped with the usual hoisting machinery.

Where the limestone strata are steeply inclined, shrinkage stoping is occasionally employed and also the glory-hole method. These methods, of course, call for more professional advice and skill than the room-and-pillar method, and are more hazardous. Nevertheless, they are employed in some operations in competition with near-by open quarries, where there are difficult stripping problems.

There are some disadvantages to underground mining, such as provision for ventilation. In some room-and-pillar mines, ventilation is easily taken care of by nature, sometimes with the help of a few boreholes from the surface. Where such ventilation is good, the mining laws of some states permit the use of gasoline-powered shovels, locomotives, and trucks. There is always a hazard of falling roof rock, and underground workers require greater skill and intelligence, and consequently are higher priced labor, than quarry workmen. Underground mining usually produces a higher percentage of fines, which is not important if rotary kilns are used for calcining.

For shaft kilns (Fig 1), experience has shown that even the most modern kilns designed to burn some of the smaller sizes or "spalls" cannot take more than 75 pct of the stone quarried and loaded. Therefore, to manufacture 100 tons of lime per 24-hr day would require quarrying approximately 250 tons of stone per day, unless only kiln-sized stone were loaded by hand in the quarry. The capacity of rotary lime kilns, as presently installed, is seldom less than 100 tons per 24 hr,

so that the problem of disposal of spalls is a most important one with the small plant operator.

PREPARATION FOR MARKET

Essentially, the manufacture of lime is a very simple operation and undoubtedly one of the very earliest arts practiced by man. Originally the calcination process consisted merely of heaps of stone or shell mixed with wood fuel and fired. Enclosure of the burning mass within walls was a natural development; and that constitutes the essentials of a "pot" shaft kiln to this day. Because the lime made in a "mixed-feed"

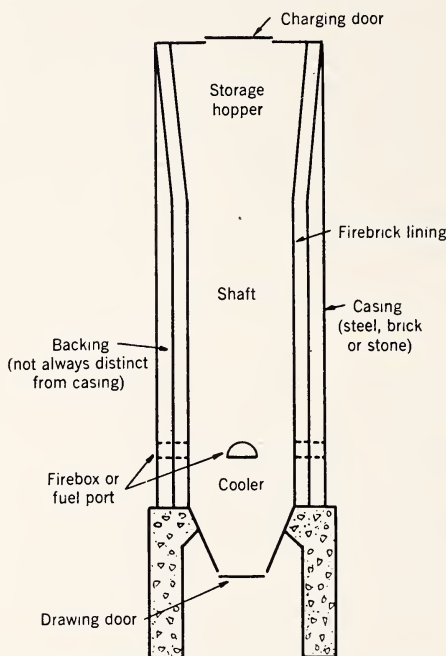


FIG 1—DIAGRAMMATIC SECTION OF SHAFT KILN SHOWING ESSENTIAL PARTS.
Reproduced from Bureau of Mines I.C. 6884R.

kiln becomes contaminated by the fuel ash, separate fireboxes replaced mixtures of fuel and limestone; later gas producers, either integral with the kiln, or separate, came into general use, because flame rather than hot gases is more effective in transferring heat to the stone.

The primary problem of lime manufacture has remained in making the most effective and efficient use of heat for both quantity and quality of product. Mixed-feed kilns, charged with alternate layers of coke or anthracite and limestone, are still the most efficient in utilization of available heat. Kilns of this type are used in some industries where the resulting contamination of the lime is relatively unimportant, and where, as in the beet-sugar industry, the carbon dioxide gas

escaping from the kilns is made use of in the processing. Burning lime in such kilns ensures complete combustion of the fuel, which adds to the amount of CO_2 gas available.

When wood was plentiful, it was the preferred fuel for burning lime, for at least two reasons: (1) it was practically impossible to "overburn" (hard burn) lime with wood; (2) it burned with long flames, which lapped around the pieces of stone in the kiln and thus provided ideal conditions for efficient transmission of heat. Most of the progress made in lime-kiln design in the recent past has been concerned largely with duplicating the action of the flames in wood burning. This has resulted in the increasing use of gas burners, for both natural and producer gas, and devices for tempering or reducing flame temperatures that normally accompany combustion of gas.

There has been much difference of opinion as to the effect of steam on the calcining of limestone. One of the advantages of wood as fuel is that considerable steam is evolved in its burning. On the other hand, combustion engineers have pointed out that steam is a great waster of thermal units, and that the same effect in tempering hot flame may be accomplished with waste CO_2 gas. However, it is common practice to use steam or water vapor in oil burners, both to reduce flame temperatures and volatilize the fuel. W. H. MacIntire, University of Tennessee, has patented a process of calcining limestone in an atmosphere of superheated steam. He found that under these conditions limestone would evolve CO_2 at temperatures more than 100°C below the usually accepted ones for dry calcination, and that the calcium and magnesium oxides resulting from the steam calcination were far more active chemically than lime burned in the ordinary way.

It was common practice in the manufacture of dolomitic finishing lime in Ohio, to use steam injectors under the grates or directly into the fireboxes, in order to prevent overburning of the magnesia component of the lime. Recent installations have substituted CO_2 for steam, with satisfactory results.

Early gas-fired kilns did not vary much from oven or firebox-fired kilns, except that they were designed to carry as much of the combustible gases as possible from the firebox into the kiln through side ports or tuyeres. When thus introduced, the gases and flames tend to hug the walls of the kiln rather than be distributed where they will do the most good. Improvements led to the design of center-burner kilns, which are now considered the most efficient in the utilization of heat (Fig 2). Tempering of flame temperature is done usually by sucking off some of the CO_2 gas above the calcining zone of the kiln and diluting the fuel gas with it. Since this CO_2 gas is at a relatively high temperature, recirculating it adds heat for the calcining process, which otherwise would be lost.

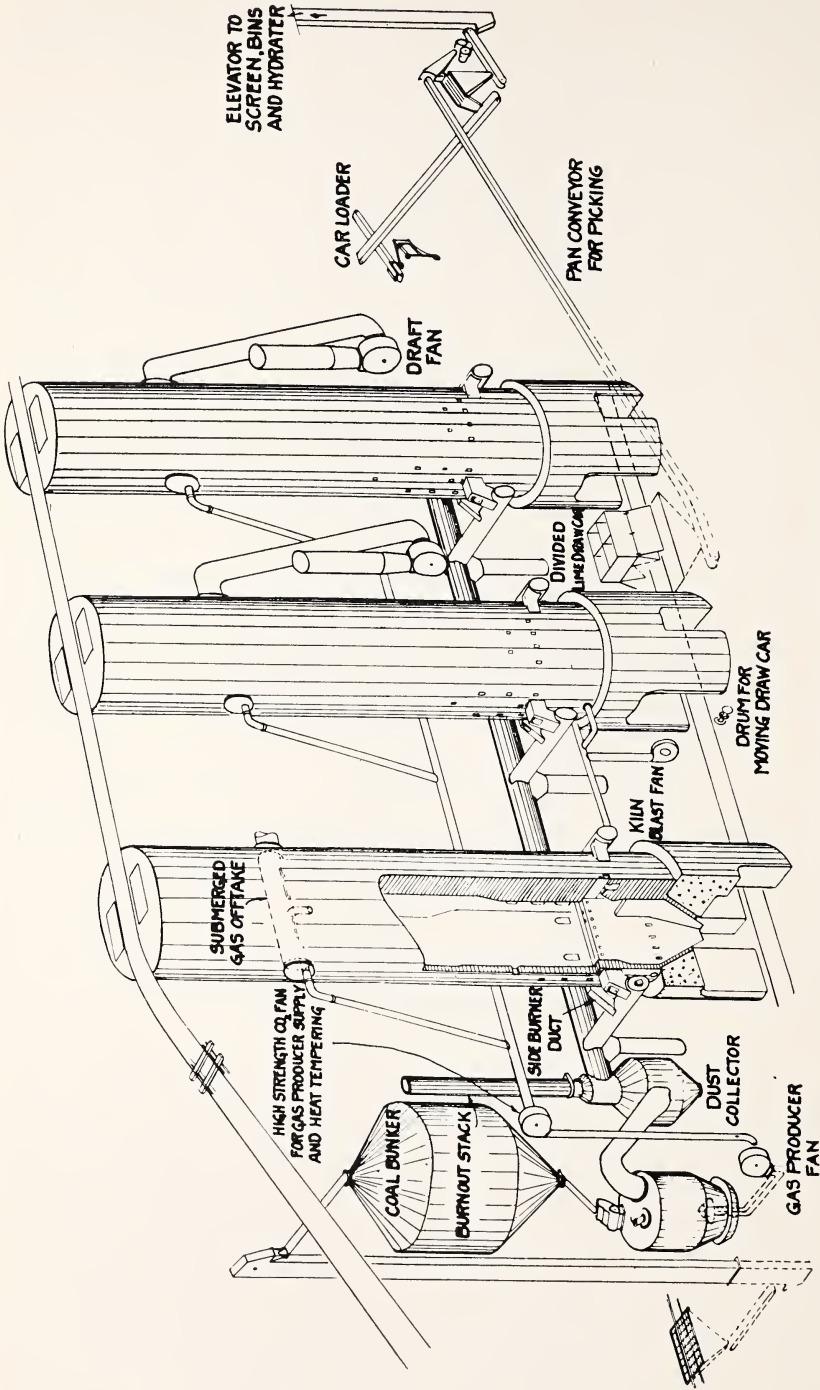


FIG 2—MODERN PRODUCER-GAS-FIRED LIME KILN.
Courtesy of Victor J. Azbe.

Efficient combustion and utilization of the heat units in the calcining or burning zone of the kiln is only one phase of the problem, however. Limestone does not begin to evolve CO_2 gas freely until a temperature of approximately 1800°F is reached under normal kiln conditions. On laboratory samples, the temperature of dissociation of calcium carbonate is about 1650°F and that of magnesium carbonate about 1400°F . The actual temperatures under operating conditions are never less than 2000° , usually between 2000° and 2500° , in order to avoid long periods that would be required to completely calcine the limestone at lower temperatures. The actual time required for a piece of rock (later lime) to travel through a shaft kiln into the lime-cooling zone has been found to vary widely in different kilns, from less than 2 days to 8 days, depending on the method of firing the kiln as well as on the kind of lime or limestone. The shorter periods are for gas-fired kilns.

The time the piece of limestone is actually in the calcining zone of the kiln is, of course, much less—a matter of hours. In order to utilize the heat escaping the calcining zone, modern shaft kilns are designed to have two more or less distinguishable zones above: (1) a preheating zone designed to bring the limestone to the calcining temperature before it enters the calcining zone; (2) an adequate, covered, stone storage zone. Since there is always more waste heat above the calcining zone than can be utilized to preheat the required amount of limestone, some of it may be recirculated as already described, which of course also provides induced draft. The proportioning of the three zones to meet specific conditions is what constitutes the art and science of shaft-kiln design.

Below the calcining zone in the kiln is a cooling and storage zone for the lime. Modern kilns are designed so that practically all the air required for combustion within the kiln is admitted through this cooling zone, or cooler, thus preheating the combustion air and reducing the heat requirement from actual combustion. The lower the temperature of the lime drawn from the cooler, the more efficient it is as a heat conservation device, and in modern kilns it is not unusual to be able to hold a piece in the hand as it is drawn from the cooler. The space provided for the cooler thus bears a very definite relation to other kiln dimensions. Practically all modern shaft kilns require induced draft, because of their height.

Operation of Kilns

Operation of shaft lime kilns follows two general practices depending on the design of the kiln, the characteristics of the limestone and of the kiln lining, and the operator's experience. Originally the shafts of kilns were walls of limestone but as these suffered from partial calcination

and abrasion it became the practice to line them with refractory brick or block. Since nearly all refractories in common use are acidic in reaction and lime is basic, there is a tendency for the hot lime to react with the lining and to stick to it. This, and the arching effect of pieces of rock in a shaft, makes a kiln "hang." This tendency is made use of in operating many kilns to draw the finished lime from the cooler and to drop the lime in the calcining zone into the cooler. The partly burned stone and limestone above where the kiln is hung is then poked down with iron bars through poke holes and firebox. The drawing and poking are done at intervals a few hours apart, when fuel supply is cut off.

The alternate method of operating a shaft kiln is called the "follow" method. The kiln is so designed that the stone and lime are expected to make steady progress through the kiln without hanging, and the lime can be drawn either continuously or at relatively short time intervals. Kilns designed to follow are usually of vertical cylindrical section with oval-shaped calcining zones. Kilns designed for the hanging method of operation are of various cross sections and much ingenuity has been displayed in attempts to achieve the desired purpose. Probably there are few shaft kilns that do not stick or hang under some operating conditions, which is another problem in combustion, involving selection of fuels and the refractory lining for the best results with a particular limestone. Under all conditions, kilns must be relined regularly.

The kiln shaft may be stone masonry, reinforced concrete or boiler plate. The boiler-plate kiln is by far the commonest. For greatest economy, a layer of insulating material is placed between the kiln shell and lining. The burners, or furnace arches, especially if center burners, are of the highest grade of refractories available. The essential elements of an ordinary shaft kiln are shown in Fig 1 and a typical modern shaft-kiln lime-manufacturing plant in Fig 2.

The capacity of shaft kilns varies widely with different designs and methods of firing and drawing, the size of the limestone fed, and other factors. For greatest efficiency, the least horizontal cross section for production of one ton of lime in 24 hr is a fair measure—stated in another way, the largest tonnage per square foot of horizontal kiln-cross-sectional area. Good performance is from $\frac{3}{4}$ to 1 ton of lime per 24-hr day for each square foot of shaft area. The efficiency may also be computed on tons produced per cubic foot of shaft volume, since this would involve also the relative efficiencies of the various zones in the kiln and their appropriateness to the overall dimensions of the kiln.

Calcination of limestone in rotary kilns probably accounts for more than half the total tonnage of lime produced in the United States at the present time. They became popular as markets developed for granulated and pulverized quicklime in the chemical industry. The use of rotaries makes possible utilization of crushed stone to about $\frac{1}{4}$ -in. size and par-

ticles up to $1\frac{1}{2}$ -in. size can be handled economically. However, because of the different time requirements involved in calcining stone of different sizes, the best practice is to segregate the sizes fed to any one kiln at one time within fairly narrow limits. When fine and coarse sizes are fed simultaneously, the fines have a tendency to sift to the bottom of the kiln segment and to remain uncalcined.

Until recently there was far less fuel efficiency in rotary kilns than in the average shaft kiln. A common fuel ratio, with pulverized coal of approximately 14,000 Btu per pound, was about 1 lb of coal to $2\frac{1}{2}$ lb of lime for a rotary kiln, against 1 to 4 or even 1 to 5 for efficiently operated shaft kilns. The introduction of preheaters for the stone ahead of the kiln, heat exchangers in the kiln, and improved coolers of various types to use preheated aid for combustion, have so improved performance of rotary kilns in the lime industry that fuel ratios are now not far behind those of shaft kilns.

Rotary kilns have the advantage of greater production per man-hour and better control of temperature and feed, which means better control of the quality of the product. Their disadvantages are a much higher investment cost and the requirement for steady operation at maximum productive capacity, which means a large and steady market. Sizes of rotary kilns vary from 6 by 60 ft to 11 by 400 ft, although kiln lengths of 150 ft are probably most common. A kiln of this size has a daily 24-hr capacity of not less than 100 tons; usually about 150 tons.

It is possible to estimate the time required for a particle to travel the length of the kiln by means of a formula developed by the Bureau of Mines in 1927 (Tech. Pub. 384), as follows:

$$t = \frac{1.77 \times \sqrt{\theta} \times L}{S \times D \times N} \times \text{Factor}$$

t = time of material in the kiln, minutes,

L = length of kiln, feet,

D = diameter of kiln inside the lining, feet,

S = slope of kiln, degrees,

N = revolutions per minute of kiln,

θ = angle of repose of the material.

The Factor in the formula is to take care of obstructions in the kiln or for changes in the diameter of different zones. For a cylindrical kiln without obstructions it would be one. Incidentally, dams or obstructions in the kiln increase its output and efficiency by turning over the stone more effectively and by increasing the turbulence of flames and hot gases, thus preventing them from "channeling" through the kiln without doing their best in heat transfer.

The efficiency of rotary lime kilns can be measured by the volume

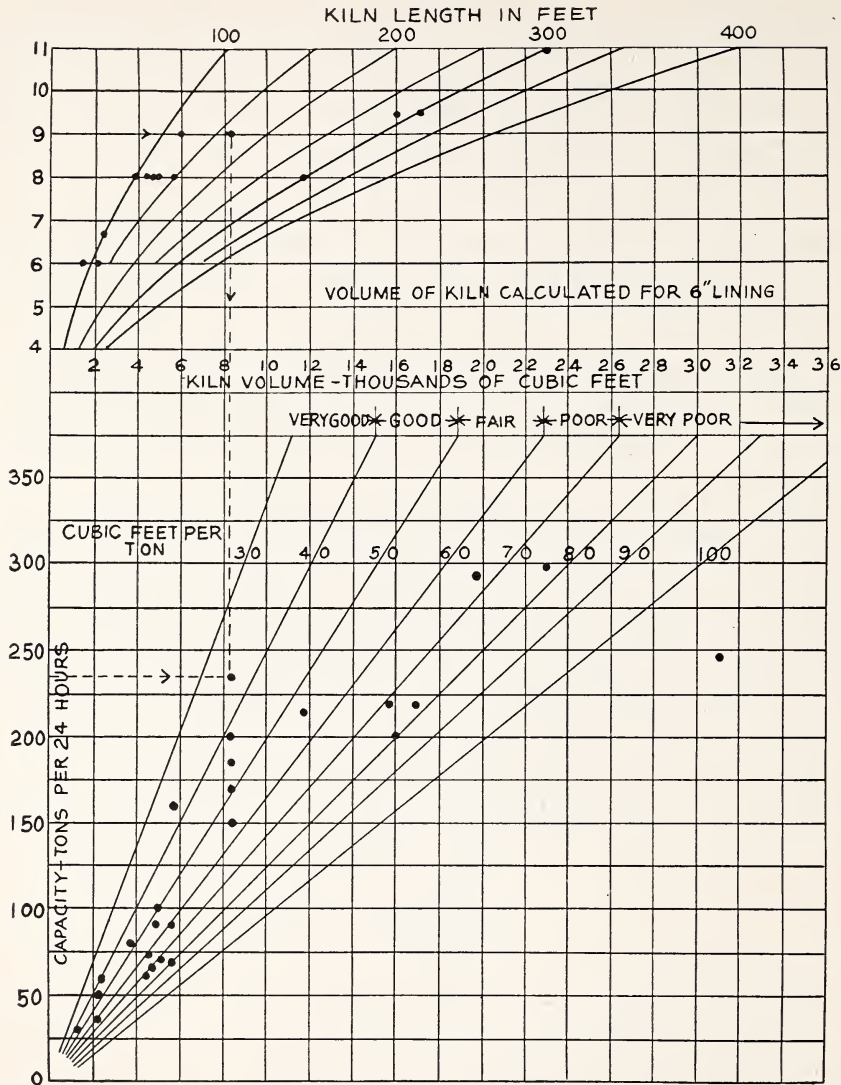


FIG 3—CURVES SHOWING RELATION OF ROTARY KILN VOLUME TO CAPACITY, BY VICTOR J. AZBE.

Reproduced by courtesy of *Rock Products*.

in cubic feet of kiln space required to calcine a ton of lime in 24 hr. Azbe has found that this varies from 30 to 70 cu ft. In other words, a kiln that produces one ton of lime for every 35 cu ft of interior volume (inside the lining) is an efficient operation, and one requiring 70 cu ft for production of the same tonnage is rated very low in efficiency. These ratings are based on production of high-calcium lime (Fig 3).

Rotary kilns, with few exceptions, are used for the manufacture of

hard-burned or sintered dolomite, classified as "refractory lime." The preparation of the dolomite for calcining includes crushing, usually with rolls, to reduce the amount of fines, and mixing with the sized dolomite a small percentage of iron ore, boiler scale, or other iron ingredient. The mixture is then calcined at sintering temperatures of about 2800°F. The product is granular and is shipped chiefly in bulk in boxcars, direct to the steel plants, for lining the bottoms of open-hearth furnaces. It is used also for the manufacture of dolomite refractory brick.

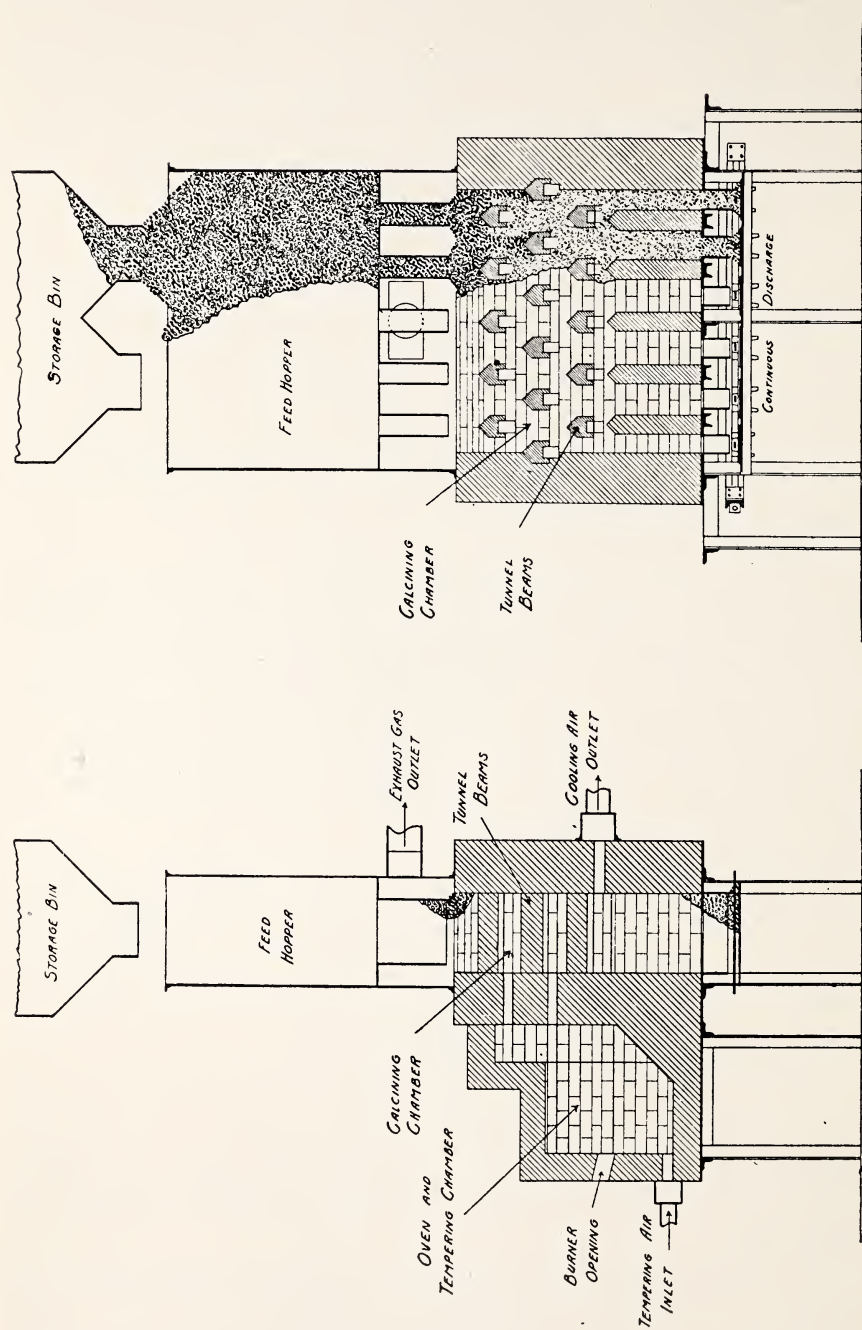
In addition to shaft and rotary kilns for calcining limestone, there are a few installations of special types, including a Dwight and Lloyd ore-sintering machine, with traveling grate and downdraft gas burners, used for sintering dolomite. Other types of ore-roasting furnaces also have been adapted for calcining limestone on an experimental scale. A special type of kiln (patented) for burning spalls, known as the Eller-man kiln, has been used in several installations. In this kiln, ribbons of limestone feed of $\frac{1}{4}$ to $\frac{3}{4}$ -in. stone dribble down from overhead pockets through narrow flues in which the flame and hot gases are rising under induced draft (Figs 4 and 5).

A recent development in lime kilns utilizes the fluid-solids principle of calcining small particles of calcium carbonate or limestone while they are maintained in dense suspension in a gaseous medium. The principle of emitting enough low-pressure air or other gas into the bottom of a bed of pulverized material to air-float or fluidize it is not new but the application to a lime kiln is novel; it resulted from a process pioneered by the Standard Oil Development Co. for regenerating mineral catalysts in the manufacture of high-octane gasoline. In the lime industry, the method is known as the Dorrico FluoSolids (patented) process, and the kiln is called a reactor (Fig 6).

As a lime kiln, the reactor is a steel cylinder lined with refractory and placed in an upright position. In other words, it resembles an ordinary shaft (vertical) lime kiln. It is divided by perforated, domed, refractory constriction plates into three or more compartments, as shown in Fig 6. These compartments correspond to the preheating, calcining, and cooling zones of an ordinary shaft lime kiln.

The limestone feed is preferably minus 10-mesh and for best results should have most of the dust removed. The feed spout extends to near the bottom of the preheating compartment. Air under low pressure enters through ports distributed at various points in the bottom constriction or diaphragm in sufficient quantity to "fluidize" and cool the lime prior to discharge.

The warm air then passes through the calcining compartment, where the fuel is injected, and the products of combustion then pass to upper compartments to preheat the limestone. As it progresses upward, the gas pressure diminishes so that in the preheating, or initial fluidizing,



Figs 4 and 5—ELLERMAN LIME KILN FOR BURNING SPALLS.

compartment, the pressure normally is less than one pound per square inch.

When the level of the dried and preheated limestone particles in the fluid-solid state rises to the top of the outlet pipe, the material flows to the bottom of the compartment below, where it is held in suspension for a period sufficient to calcine these small particles of carbonate. This time depends on the size and other properties of the particular material,

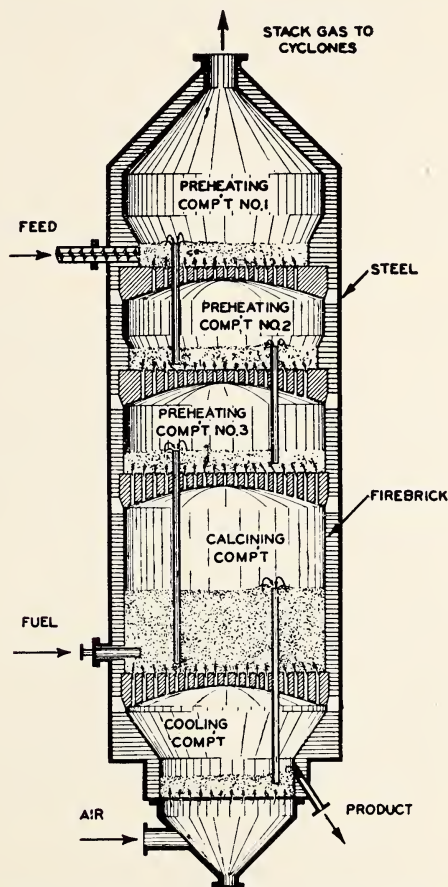


FIG 6—FLUOSOLIDS REACTOR ADAPTED TO CALCINING PULVERIZED STONE.

and of course is controlled both by the fuel supply and temperature and the rate of feed of the carbonate. The lime particles overflow into the pipe leading to the bottom of the next compartment or to the cooler compartment.

Fuel to lime ratios with fuel oil have been 1:5 and 1:6 as compared with a coal having 14,000 Btu per pound. The advantage, however, is not entirely in fuel economy. Because of the relatively low temperatures

at which these small particles of limestone may be calcined (about 1800°F), the lime made in this kiln has peculiarly active properties. The kiln controls are so regulated that any type of lime can be made but its best economy probably is obtained in the manufacture of quick-acting chemical lime. Because of the absence of moving parts and localized overheating, it is expected and experience thus far has shown that refractory maintenance will be low.

Kilns of this type have been manufactured to calcine about 100 tons of lime per day, at an installation cost below that of a rotary kiln of the same capacity. However, operation of the kiln requires expert supervision and control; and the operation involves a dust loss of between 5 and 10 pct when burning a suitable limestone. It is possible that some limestones dust too readily to be calcined by this process. The dust collected from the top compartment of the kiln in a suitable device for that purpose is substantially calcium carbonate and is a marketable product.

Handling the Product

The calcined product of any kind of lime kiln may require careful selection or hand picking in preparation for the markets, to avoid "core" or pieces of uncalcined rock. This is particularly true of the product of shaft lime kilns, for which it is common practice to spread the drawn lime on the floor of the shipping room or shed and inspect all large or suspicious pieces by breaking them up with a hammer. A more modern method is to inspect and hand-sort the lumps as they pass between two workmen on opposite sides of a picking conveyor.

Lime is prepared for the market in the following forms: (1) large lump, 8 in. and smaller; (2) pebble or crushed, $2\frac{1}{2}$ in. and smaller; (3) ground, screened or granular, $\frac{1}{4}$ in. and smaller; (4) pulverized, substantially all passing a No. 20 (840-micron) screen; (5) standard hydrated lime; (6) superfine hydrated lime. The first requires no preparation except packing in barrels or similar containers; the second, pebble lime, is usually a lime that naturally disintegrates to pebble or granular size in the kiln; crushed lime is lump crushed to pebble or granular size; pulverized lime is lump or granular lime reduced to powder, usually in a hammer or ring-roll mill, with screen or air separation. Pulverized quicklime and hydrate are difficult to screen through fine meshes because they are repulsed from steel wire by an electrostatic charge, which builds up on the particles.

Mechanical hydrators are made in various designs, both for batch and continuous processing (Figs 7 and 8). The lime is usually crushed and the water fed to it slowly while the mixture is agitated to permit the water to reach as much lime as possible quickly. The simplest hydrator is a pug mill. Water and lime must be accurately proportioned and some water is lost in the form of steam. This water and the dust that

escapes with it may be recovered in spray-type dust collectors and this suspension of fine lime hydrate in water may be re-used in the hydrator. After hydration, the product usually is put through a hammer or ring-roll type of mill equipped with an air separator. The uncalcined material and particles of lime combined with silica and alumina, being less easily pulverized, are rejected by a throw-out device in the lower part of the mill. By manipulation of the air separator, hydrate of various finenesses may be made, the very fine, usually below the No. 300-mesh size of particle, is commonly sold as "superfine" hydrate.

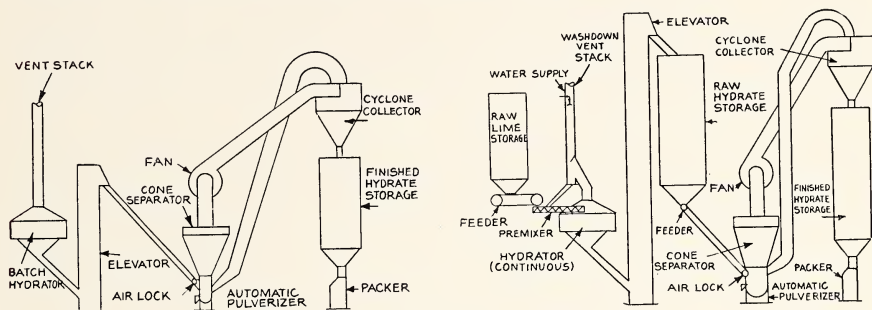


FIG 7—SIMPLE FORM OF HYDRATING SYSTEM.

Consists of a Clyde batch hydrator, automatic pulverizer, cyclone collector, and storage bin for finished hydrated lime, with packing facilities.

FIG 8—ANOTHER SIMPLE FORM OF HYDRATING SYSTEM.

Hydrating system similar to that in Fig 7 but with batch hydrator converted for continuous operation and bin for storage of raw hydrate between hydrator and automatic pulverizer.

Carbon dioxide gas (CO_2) is the chief waste by-product of commercial lime plants, since it comprises almost half of the raw material. It can be recovered, purified and compressed into liquid or solid form, and this is done at a very few lime plants. The investment cost is high, skilled labor is required and there are commercial difficulties in marketing the finished product. However, it is feasible under favorable conditions.

TESTS AND SPECIFICATIONS

Limes vary widely in their physical characteristics and these variations are often as important for chemical and industrial purposes as the chemical analyses. In some instances, the physical characteristics can be modified by the method or degree of calcination and the hydrating process selected; in others, they appear inherent in the raw material. Therefore, tests and specifications are designed to provide for a particular lime product that has been found by experience to give consistently satisfactory results in some one or more industrial processes. Because of these facts it has not been possible to write an overall specification for

chemical lime, although the project has been under study for several years by the Lime Committee of the American Society for Testing Materials.

Some of the physical factors that determine the suitability or unsuitability of lime and hydrate for various industrial applications include: (1) settling rate of high-calcium hydrate suspensions; (2) settling characteristics of dolomitic lime hydrates; (3) surface areas; (4) abrasiveness; (5) hydrate adhesion; (6) microscopic texture; (7) electrostatic charge. Settling rate of suspensions of high-calcium hydrates is of great importance in many industrial processes. Some industries—for instance, paper manufacture—require quick-settling limes in order to avoid delays in recovery of the liquor. Leather treating and numerous other processes require slow-settling lime.

The settling rate and the volume of the precipitate appear to be affected by various factors. Hard burning apparently speeds the settling rate. The temperature of the hydrating water, or of the hydrate suspension, is also a factor, and the use of excess water up to a certain point, which reduces the temperature, gives a slower settling rate. The settling rate is also affected by size, shape and porosity of the lime particles. Chemical analysis of the lime does not appear to be an important factor. Various wetting agents help or hinder the settling rates. Separation of the finest particles by air separation, as in the preparation of superfine hydrates, makes possible production of limes with slow settling rates. Manufacturers of lime, therefore, have to vary their burning and hydrating processes to meet the demands of their different customers. Usually, better control of the product is possible with a rotary kiln than with a shaft kiln.

With dolomitic hydrates, it is more difficult to change characteristics by control of burning and hydrating processes. Some dolomitic limestones burned at progressively higher temperatures become faster settling and show smaller settled volumes. Other dolomites make slower settling hydrates and larger putty volumes when burned at 2500°F for long periods. Since dolomitic limes are used largely for construction purposes, it is the settled volume, or putty volume, that it is desired to increase to a maximum, and apparently each lime must be studied separately to achieve the desired results.

The specific surface area of the lime-hydrate particles is an index of its relative activity and usefulness for some purposes. The surface area takes into account both particle shape and porosity. It is difficult to measure except by the use of an absorption test using nitrogen or other inert gas or liquid. For water treatment, bleaching-powder manufacture, the soda-lime process, and other uses, surface area is a very important consideration because involved with it is "the available calcium oxide." The surface area determines the surface exposed to the liquid and is important in any process in which rapid reactions are

desired. Probably it can be controlled to some extent by the methods and temperatures of burning and hydration.

The abrasiveness of lime is significant for some uses; such, for example, as wire drawing, where it is intended to serve as a lubricant. In any process in which a suspension of lime in water (milk of lime) is pumped through pipes and valves, an abnormally abrasive lime may be costly because of frequent replacements of equipment. This includes lime used in agricultural insecticide sprays. There is a wide variation in the relative abrasiveness of lime hydrates, caused apparently both by the nature of the stone and its impurities, and in the preparation of the hydrate. Hard-burned limes, because of chemical combination with silica and alumina, tend to be more abrasive than soft-burned limes.

Hydrate adhesion or the bonding of the hydrate to metallic surfaces is a factor in some industries; as, for example, in wire drawing. Hydrates vary widely in this property. In some wire-drawing plants, it is customary to allow the wire or rods to rust slightly in order to improve the adhesion.

The texture of the lime-hydrate particles is involved in nearly all the foregoing properties, and this has been studied by both the ordinary microscope and the electron microscope. The particles usually are in the 0.5 to 5.0-micron range and apparently are flaky, tending to pack readily. The harder the burning, the thicker the flakes appear to be. Even with the electron microscope, it has not been possible to identify crystals.

The ability of pulverized lime and dry hydrate to acquire and hold electrostatic charges has been observed in many instances and is troublesome in screening and conveying. It causes an otherwise free-flowing product to ball up and arch in chutes or otherwise clog the equipment. This property may possibly be a factor in some uses for lime but very little is known about its causes or cure.

The Federal Government and the American Society for Testing Materials have published specifications for lime and hydrated lime for various uses. Those of the ASTM are readily available at a small charge to cover cost of printing and mailing. These specifications are under constant review and revision and at this writing (September 1947) are being studied with the possible end in view of writing a single overall specification with explanatory notes to cover special applications.

Existing ASTM specifications are as follows: C5-26, Standard Specifications for Quicklime for Structural Purposes; C141-42, Standard Specifications for Hydraulic Hydrated Lime for Structural Purposes; C45-25, Quicklime and Hydrated Lime for Cooking of Rags in Paper Manufacture; C46-27, Quicklime for Sulfite Pulp Manufacture; C47-27, Hydrated Lime for Varnish Manufacture; C48-24, Quicklime

and Hydrated Lime for Use in the Textile Industry; C49-42, Quicklime and Hydrated Lime for Silica Brick Manufacture; C53-39, Quicklime and Hydrated Lime for Water Treatment; C50-27, Standard Methods of Sampling, Packing, and Marking of Quicklime and Lime Products; C25-44, Standard Methods of Chemical Analysis of Limestone, Quicklime, and Hydrated Lime; C51-44, Standard Definitions of Terms Relating to Lime.

In addition to the Standard Specifications listed, Tentative Specifications are available as follows: C6-46T, Normal Finishing Hydrated Lime; C206-46T, Special Finishing Hydrated Lime; C207-40T, Hydrated Lime for Masonry Purposes; C110-45T, Tentative Methods of Physical Testing of Quicklime and Hydrated Lime; C51-44T, Tentative Definitions of Terms Relating to Lime. Tentative Standards are those in the process of becoming standard and are subject to yearly revision or recall. While the standard and tentative specifications issued by the American Society for Testing Materials by no means cover all the industrial uses of lime, they are the most reliable source of information on some of the special properties of lime sought for by different classes of industrial users.

Aside from improvised tests for the physical properties of lime and lime hydrate referred to in the earlier part of this section, for industrial and chemical uses, the main interest in physical testing has had to do with lime for construction purposes. These tests are designed to determine the residue on a No. 30-mesh and a No. 200-mesh standard testing sieve. A 100-gram sample is washed through the sieve in a stream of water. Consistency of lime putty is determined in a modified Vicat apparatus, using the penetration of a plunger of 12.5-mm diameter instead of the "needle" used in cement tests. This is primarily a test to find the water-requirement properties of a lime putty.

The plasticity of the putty is determined by a special device invented by Warren E. Emley, National Bureau of Standards, known as a plasticimeter, which measures the slip of a smooth, horizontal, revolving disk on a pat of lime putty resting on a porous porcelain base plate. The disk revolves slowly (one revolution in 6 min. 40 sec), and the plate holding the lime putty moves upward $\frac{1}{13}$ in. with each revolution of the disk. Measurement of the torque required to turn the disk is the reading used for estimating the plasticity of the lime putty, according to the formula:

$$P = \sqrt{F^2 + (10T)^2}$$

where P = plasticity figure,

F = scale reading at the end of the test,

T = time in minutes from the time the first portion of paste was put in the mold (base plate) to the end of the test.

The disk is started revolving 120 sec after the first portion of the paste is put into the mold. The disk continues to revolve until: (1) the scale reading reaches 100; (2) any reading is less than the one before; (3) the scale reading remains constant for three consecutive readings (2 min.), and the specimen has visibly ruptured or broken loose from the base plate.

The soundness of hydrated lime is tested by mortar pat specimens made up with natural Ottawa silica sand, cured in a damp closet for 24 hr then covered with a thin layer of lime paste and stored again in a damp closet for 24 hr. The specimen is then examined for cracks or "pops"; subsequently the pat is suspended in a vessel above water level and the water is boiled gently for 5 hr. This test is designed to accelerate the effect of any hard-burned, unhydrated particles, which in the course of the test will hydrate and swell, thus giving evidence of unsoundness in the lime sampled.

A more severe autoclave test for soundness has been given considerable prominence in recent years, especially by the National Bureau of Standards, which holds a theory that failures of lime plaster have been caused by the unhydrated magnesia content of dolomitic limes. Consequently, some specifications require that the unhydrated oxides in hydrated lime shall not exceed 8 pct, or even 5 pct. It is probable that unhydrated particles of calcium oxide are just as important in unsound mortar and plaster as the unhydrated magnesium oxide. This specification requirement has led to special processes of hydration (most of them patented) and to greater care in burning to avoid hard-burned lime.

Since the value of lime in mixtures of portland cement, lime and sand is based largely on the capacity of the lime for retention of water, thus providing plasticity and workability and proper moisture conditions for hardening and curing, various tentative tests have been proposed to determine and compare this physical property of hydrated limes. According to the present tentative method of the ASTM, a special piece of equipment is required, which measures the flowability of the mixture after the amount of water that can be sucked out of a mortar specimen in one minute is removed. Other methods suggested include an extrusion device for testing the plasticity or flowability of the mortar.

Chemical tests of lime and hydrated lime are designed primarily to determine the amount and character of the minerals that are insoluble in dilute hydrochloric acid (HCl). Separate tests are then made to determine the percentages of silica, alumina, and iron, the three common impurities. For many purposes, that is as far as chemical analyses need be carried. Where more complete analytical work is necessary, the best source of laboratory technique is the Analysis of

Silicate and Carbonate Rocks, *Bull.* 70 of the U. S. Geological Survey. Because of the increasing importance attached to "trace" elements in the metabolism of plants and animals, it is desirable that the producer of agricultural lime and limestone have as complete an analysis of his material as can be obtained. It is also important where the product is used directly in animal-food mixtures or in processing human-food products such as baking powders.

Typical specification requirements for lime to be used in industry, based on standards of the ASTM, are as follows: In general, the minimum amount of calcium oxide in a high-calcium lime must be 93 pct; where a dolomitic lime is permissible, the combined calcium and magnesium oxide content must be not less than 94 pct. In a high-calcium lime, the maximum percentage of magnesium oxide is 5. Silica in both types of lime usually is limited to 2.5 pct; iron and aluminum oxides to 2.5 pct, and the total $\text{SiO}_2 + \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ to 4 pct. The available lime, determined preferably for the particular use, must be a minimum of 86 pct. When hydrated lime is used, the oxide contents are computed on an ignited or nonvolatile basis; that is, independent of the water or carbon dioxide content. Some industrial users require higher minimums. Specifications usually require that quicklime and hydrate shall not contain more than 3 pct carbon dioxide, and quicklime not more than 2 pct combined moisture, or hydrated lime more than 1.5 pct mechanical or free moisture. It is important to the lime manufacturer, therefore, that the specifications describe where the samples are to be taken—at the lime plant or the receiving point—and provide for proper protection of the samples awaiting test.

Special Uses

Rag-paper Manufacture—Lime is used in cooking rags in a steam-pressure digester, either with or without soda ash. On samples taken at the place of manufacture, the lime must have a minimum of 90 pct CaO; hydrated lime, 64.3 pct (equivalent to 85 pct $\text{Ca}(\text{OH})_2$). For the determination of "available CaO," either the hydrochloric acid test or what is known as the rapid sugar test (ASTM C25-44) is used. The sugar test consists of boiling for 2 min. a sample of lime in a solution of 15 grams of granulated sugar in 150 ml of distilled water.

Sulphite Pulp Manufacture uses lime in suspension in water as "milk of lime." The function of the lime is to absorb sulphur dioxide, drawn or forced through the milk of lime, the lime serving as a base for the formation of calcium and magnesium bisulphides. Either high-calcium or dolomitic lime may be used but it is important that the ratio of MgO to CaO remain fairly constant. If high-calcium lime is used, the quantities are: 92.5 pct CaO, 2.5 pct maximum MgO and 3.0 pct maximum SiO_2 , Al_2O_3 , Fe_2O_3 impurities; with dolomitic lime, 55.4

pct CaO and 39.6 pct minimum MgO is required, with the same limit on impurities.

Varnish manufacturers require about the purest high-calcium lime commercially obtainable. It is used in the form of a hydrate in making oleoresinous varnishes, to harden and partially neutralize the resin. About 8 lb of hydrated lime is added gradually to 100 lb of melted resin and heated for a short period. The hydrate used must be white or colorless, completely hydrated, and not more than 10 pct should be retained on a No. 230 (62-micron) sieve. The calcium oxide on a nonvolatile basis must be a minimum of 94 pct and the magnesium oxide a maximum of 3 pct. Other impurities and insolubles are limited to 3.4 pct, including iron oxide, which is limited to 0.4 pct because of its coloring properties. Carbon dioxide is limited to 3 pct if the sample is taken at the place of manufacture and to 5 pct if taken elsewhere.

A special test is applied to determine the reactivity of the lime for this particular process; that is, the tung-oil heat test (ASTM C47-27), which consists essentially of stirring a 1-gram sample of hydrated lime into 50 grams of raw tung oil and heating. High-quality lime will usually start to react at about 80°C, small bubbles rising to the surface. As heating is continued, large flakes of lime tungate form and rise to the surface and the oil below becomes fairly clear when a temperature of 120°C is reached. A poor lime will fail to react as described.

In the textile industry, specifications for lime require a high-calcium lime with a limit of 3 pct MgO and 2 pct Fe_2O_3 plus Al_2O_3 impurities. Silica and insoluble matter together are limited to 2.5 pct and the CO_2 limits for hydrate are the same as those given for lime in the varnish industry. Either quicklime or hydrated lime may be used in the textile industry. Where quicklime is specified, the CO_2 content may be up to 5 pct when the sample is taken at the lime plant and up to 10 pct when taken elsewhere.

Municipal water-treatment plants are among the largest users of quicklime and hydrated lime. Specifications of the ASTM require high-calcium limes with not less than 90 pct CaO, or hydrate of 90 pct $\text{Ca}(\text{OH})_2$. The lime is used alone or with iron sulphate or aluminum sulphate to produce a precipitate, which assists in the clarification of the water and removal of bacteria by subsequent filtration. An excess of lime is used sometimes to remove part of the hardness of water; lime and soda ash are used together for softening water. The only useful ingredient of the lime is the CaO content and the usual water-works specification places a penalty on lime with an excessive content of insolubles (silica, etc.) and a premium on lime having less than the specified maximum percentage.

Chemical Industries—The foregoing paragraphs cover some of the pertinent details of specifications for lime in a few of the major proc-

essing industries. In general, lime for chemical industries is divided into two categories: (1) regular; (2) selected. For many processes, a minimum of 90 to 93 pct calcium oxide is sufficient—that is, “regular” lime; for some processes, a minimum of 95 pct calcium oxide is required—the “selected” limes. Similarly, the maximum magnesium oxide is limited to 5 and 2 pct, respectively. The total iron and aluminum oxides may be 2.5 pct in “regular” and 2.0 pct in “selected” lime; the total insolubles, including silica, 4 and 3 pct, respectively; the available lime, 86 and 92 pct. With hydrated lime, fineness of particle size is equally important. “Regular” hydrate will have a screen analysis something as follows: passing No. 100-mesh, 95 pct; passing No. 200-mesh, 90 pct; passing No. 325-mesh, 80 pct.

A “superfine” hydrate such as that ordinarily required for varnish manufacture would have a screen analysis approximately as follows: passing No. 100-mesh, 99 pct; passing No. 200-mesh, 98 pct; passing No. 325-mesh, 97 pct.

Purchasers’ specifications covering sampling of lime usually require samples of 100 lb for each 30 tons of lime (an average boxcar load). When bulk material is being loaded, the samples are taken at regular intervals from the conveyor or loading chute. For packaged lime, ASTM specifications provide that at least 2 pct of the packages shall be sampled, and in no case fewer than five packages shall be sampled. The contents of the packages are placed in a heap and the test samples are taken after all lumps have been reduced to pass a 1-in. ring. Sampling of bins, piles, and cars may be done by taking a core not less than 1 in. in diameter with a sampling tube driven in sufficiently to permit a fair sample, in at least 10 different parts of the mass.

The ASTM specifications (C50-27) provide for shipment of lump lime in bulk, wooden barrels, or steel containers holding 180 lb or 280 lb net, or in pasteboard containers holding 90 lb net. The two weights given for net barrels are the standards established by federal law. Pulverized lime may be shipped in bulk, in carload lots, or in cloth or paper (waterproofed) bags. Hydrated lime may be shipped in cloth bags holding 100 lb net or in paper bags holding 50 lb net. Hydrated lime is also packed in 5-lb, 10-lb, and 25-lb packages for the retail trade.

MARKETING AND USES

The manufacturer of lime has three primary market outlets: (1) building construction; (2) industrial; (3) agricultural (Figs 9 and 10). In the first, his product is distributed through building-supply dealers within an economical shipping radius of his plant. This limited shipping zone is determined both by competition and the special properties of the lime. Ohio dolomitic finishing-lime hydrates, because of their

plasticity and whiteness, are shipped countrywide for use in plaster finish coats. On the other hand, normal shipping zones for ordinary building lime are quite limited and there is much overlapping in competitive territories.

In the building construction market, lime usually is retailed by the dealer to masonry and plastering contractors in the original manufacturer's package, which is not recoverable except in rare instances where special metal containers are used. Sometimes lime is shipped direct from the manufacturer to producers of lime putty, who have

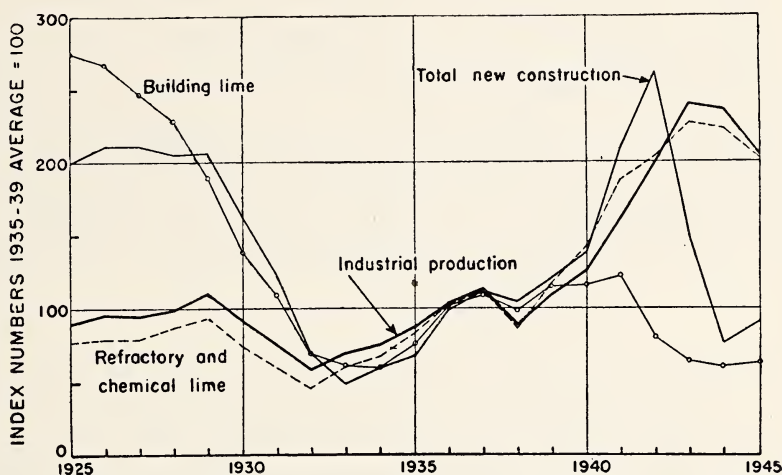


FIG 9—SALES OF REFRACTORY AND BUILDING LIME COMPARED WITH TOTAL NEW CONSTRUCTION AND INDUSTRIAL PRODUCTION, 1925-1945.

From Minerals Yearbook, 1945, U. S. Bureau of Mines. Units are reduced to percentages of the 1935-1939 average. Statistics on value of construction from the Bureau of Foreign and Domestic Commerce and on industrial production from the Federal Reserve Board.

special processes for making and handling "aged" lime putty. This putty is hauled to the building site either in steel containers or in bulk in agitator-body trucks like those used for delivery of ready-mixed concrete, frequently already mixed with sand into mortar. Where the putty alone is delivered, it is dumped in a heap, covered with sand, and used as required in the mortar mixer with the proper proportion of portland cement added.

In the industrial markets and chemical processing generally, including water purification and treatment of trade wastes and sewage, the lime manufacturer usually is faced with relatively few but steady customers for fairly large tonnages. For smaller industrial purchasers, distribution is sometimes direct from the lime manufacturer and sometimes through a broker or jobber, who may represent more than one

manufacturer. While competition for such industrial business is keen, processors are generally reluctant to change from one lime to another after having standardized their processing to suit lime from a particular source; hence there is a good deal of cross-hauling in sales territories that normally, by the uninitiated, would be considered as definitely belonging to one or two local manufacturers.

Agricultural lime in some few instances is shipped direct to farmers that use large quantities but most of it is shipped in bulk, or in paper

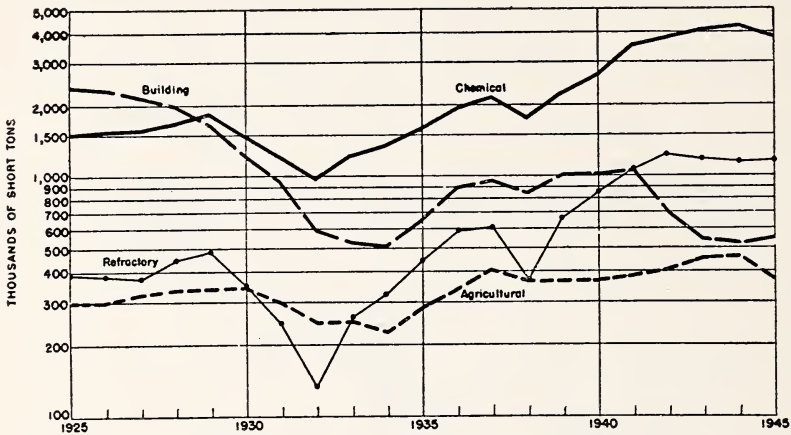


FIG 10—TRENDS IN MAJOR USES OF LIME, 1925–1945.
From Minerals Yearbook, 1945. U. S. Bureau of Mines.

packages as hydrate, and distributed through agricultural cooperatives, feed and fertilizer dealers, and building-supply dealers. Markets for agricultural lime are limited mostly to the eastern states, where farmers have used lime in preference to pulverized limestone for generations. In the central states, very little agricultural lime is used, the choice being liberal applications of relatively coarsely ground limestone. Lime and hydrate are more active in bringing about soil reactions and a smaller quantity is used in an application, but the applications have to be made more frequently. There are other uses for lime and hydrate on the farm; for instance, it is mixed with manure to preserve the nitrogen and is used for white-washing stables and hen houses, for which ground limestone cannot be used.

Ordinarily, the manufacturer is not much concerned with the quality of lime used for application to the soil and it offers a ready market for material that might be rejected for industrial and chemical purposes. However, there are scientific methods of comparing the relative soil-neutralizing values of one lime with another and with ground limestones of various fineness of particle size. Neutralization of acid soils for certain crops, however, is only one of the functions of lime in

agriculture. Primarily, it supplies the element calcium, which is a most important plant food. From this angle, hydrated lime is the most concentrated form of agricultural lime; in other words, the percentage of calcium compared with that of the other ingredients is greatest.

To market lime to be used in chemical and industrial processing requires some fundamental knowledge of the functions of lime in these processes. Only if the manufacturer is informed can he progress in improving his product or products for the particular uses. This fact has been an important influence in reducing the number of small manufacturers of lime and concentrating this phase of the industry in the hands of a relatively few large producers. The National Lime Association has taken a leading role in developing such information through original research but the files of chemical magazines show the widespread interest in independent research on lime used in processing. The following paragraphs give only a very brief discussion of a few of the important markets for lime in industry. This is designed to give some idea of the multitudinous uses of lime, but its different specific functions are fairly well covered in the processes selected.

Iron and Steel

Lime is used as a basic flux to remove carbon, phosphorus and other acid impurities from iron and steel. In blast furnaces, limestone is more commonly used. The amount of lime depends on the open-hearth furnace charge and the amount of impurities. For 55 to 60 tons of steel scrap or pig iron, 8 to 10 tons of lime is the usual amount. Limestone may be used with the pig iron but lime is usually preferred for scrap. Electric furnaces producing the highest grades of steel invariably use lime in preference to limestone. In both types of furnace, the control of the final composition of the metal is more easily accomplished when lime is used and the time required for the processing is less, because when limestone is used it must be converted to lime in the furnace before it becomes effective.

There are no general specifications for lime in the iron and steel industry but high-calcium lime with the least amounts of sulphur and silica impurities is what the process calls for. Some purchase requirements make deductions in price for silica over a certain percentage because correspondingly more lime is required. Since lime is used in large amounts in steel plants, both in the metallurgical processing and in other capacities, such as wire drawing and neutralization of pickling liquors, the nearest source of a suitable product is the one usually chosen. Like other large and steady customers, the prices paid are generally below the normal prices for the commercial product.

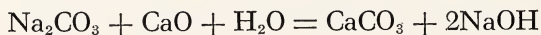
Paper Manufacture

The specifications for lime for cooking rags in paper manufacture and an outline of the sulphite process have been touched on but this is only one of several uses of lime in the paper industry. Because this industry is one of the largest consumers of lime, it is also one of the largest manufacturers of noncommercial lime. Much of the lime used in the processing is recoverable as calcium carbonate sludge, and several paper manufacturers have installed rotary kilns to burn this by-product with small additions of fresh limestone.

In the sulphite process of wood-pulp preparation, the wood chips are digested in an acid liquor and lime is used in the production of this liquor, as already outlined under Specifications, to form the soluble bisulphite salts. Magnesium limes usually are preferred because the bisulphite magnesium salts are more stable and soluble than the corresponding calcium salts; and magnesium limes are said to produce a whiter and softer pulp. Gritty impurities are objectionable.

In the soda process, the pulp is digested in a caustic soda solution; after processing, the pulp is washed free of impurities and foreign materials. Lime is not used directly in this process but is required for making the caustic soda, which the paper manufacturer may purchase or produce. In all instances, lime is used to recover the excess of caustic soda contained in the wash water obtained after digestion of the pulp.

This wash liquor is concentrated by evaporation until it carries sufficient organic matter to be "burned," producing a mixture of sodium carbonate, unburned carbon, and mineral matter from the wood. The soda from this "black ash" is leached out and sufficient new sodium carbonate is added to bring the liquor to the required strength. The mixture is then causticized—that is, converted to sodium hydroxide—by the addition of lime, according to the reaction:



The solution of sodium hydroxide is decanted or put through a filter press, to remove the calcium carbonate precipitate and impurities. This is the material burned by some paper manufacturers to re-use as lime. The mineral impurities, of course, have a tendency to build up.

The sulphate process of pulp digestion is similar to the soda process except that sodium sulphate is used in place of soda ash. New sodium sulphate and sawdust are mixed with the "black ash" before burning, leaving an ash of sodium sulphate, sodium carbonate, and sodium sulphide gained from reduction of the sulphate. This ash is leached and causticized as in the soda process.

Either quicklime or hydrate can be used but quicklime, because of the greater relative amount of CaO , is generally preferred. The mini-

imum requirement is 85 pct CaO, with as little magnesia as possible. A quick-slaking, quick-settling lime is desired. The paper industry has always been a good market for lime but the market has been subject to large losses because of the shifting locations of paper mills caused by exhaustion of all locally available pulpwood. Thus New England lime manufacturers have had their markets restricted in recent years.

Other Important Uses

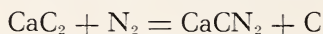
Water Supplies—The use of lime for treatment of municipal water supplies offers a large and expanding market. The lime serves both as a coagulant in the removal of impurities and as an aid to softening "hard" water. While the methods of treatment vary somewhat, the essential features of the processing involve preliminary settling of the water in reservoirs after addition of lime, lime and iron sulphate, or lime and alum. By coagulation, the impurities are removed as sediment. The clear water may then be softened by adding lime or lime and soda ash. The chemistry of the softening process depends on the fact that the calcium and magnesium salts held in solution in hard water are so held by dissolved carbon dioxide. The addition of lime removes the dissolved CO_2 and precipitates the calcium and magnesium carbonates, although additional lime may be required to convert the MgCO_3 to $\text{Mg}(\text{OH})_2$, which is less soluble than MgCO_3 . When the sulphates of calcium and magnesium are present, soda ash or sodium carbonate must be used in addition to lime to convert these sulphates to carbonates. The sodium sulphate left in solution does not cause hardness of water. The specifications for lime used in treatment of water have already been given.

Treatment of Leather—The manufacture of leather from animal hides is an example of an ancient use of lime that has never been entirely superseded, although other processes are now used. The process involves complicated reactions of alkalies, enzymes and bacteria, not any too well understood, but lime has been found by long experience to serve best in the dehairing or depilation of hides without destroying the hair, which is a valuable by-product. Either quicklime or hydrate with not less than 85 pct available CaO is required. The lime must make a fine, smooth putty and be extremely slow settling, as it is used in suspension or solution.

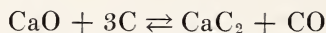
Carbide and Cyanamide—Calcium carbide and cyanamide manufacture is a large and growing consumer of lime but much of it is of captive tonnage production. Carbide is one of the chief raw materials in the manufacture of some kinds of synthetic rubber and other organic chemicals and cyanamide has become one of the major fertilizers, sometimes called "lime nitrogen" (CaCN_2). Treated in autoclaves with steam pressure, the following reaction takes place:



Calcium carbide is made by heating a mixture of lime and carbon, the latter in the form of coke, charcoal, or anthracite, to a very high temperature, or by heating limestone in an electric furnace with coke. The calcium cyanamide is made from the carbide by treating the fused carbide at 1000°C with nitrogen obtained from liquefying air; i.e.:

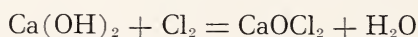


The lime serves in several ways. Sometimes it is used in the azotization process to catalyze the association of nitrogen; also to remove CO_2 from and dry the air in the liquidizing process, but chiefly in the synthesis of the carbide from the lime and nitrogen, as an oxidizing agent whereby the carbon is changed to carbon monoxide according to the reversible reaction:



High-calcium lime is required for manufacture of carbide. The amounts of silica, iron, sulphur, and alkali are not important but very low phosphorus and arsenic contents are necessary to avoid explosion of acetylene. Also, the magnesia and alumina percentages must be low, to avoid thickening of the molten carbide and the formation of crusts.

Calcium Hypochlorite—The manufacture of calcium hypochlorite (CaOCl_2) is another chemical industry in which lime enters the finished product, which is known in the trade as bleaching powder, chloride of lime, chlorinated lime, and others. It is made by the action of chlorine gas on hydrated lime, according to the reaction:



Aside from its use as a bleach, the product is in demand as a sterilizing and disinfecting agent. Large waterworks now use liquid chlorine, since it is the chlorine that makes the product useful, but for small users, calcium hypochlorite provides a convenient means of fixing and storing chlorine for many industrial and household uses. A high-calcium lime containing not less than 92 pct CaO is demanded.

Textile Manufacture—Textile manufacture involves one of the oldest industrial uses of lime, employing four distinct operations: (1) boiling out, (2) bleaching, (3) kier liming, (4) dyeing. Textile manufacturers also use lime for softening water, for making mercerized caustic, and for recovering waste lyes. In the boiling out or scouring process, lime functions as a saponifying, hydrolyzing, neutralizing, and emulsifying agent. Through its use, the fibers are cleansed of waxy coating, starch, the tannins, pectin bodies, motes, and possibly some of the oily and resinous impurities, in order to make effective the

subsequent processes of bleaching and dyeing. The bleaching requires chloride of lime prepared as already described. Dyeing processes require the use of lime as a mordant, or an alkali and precipitating agent, for fixing the metallic salt upon the fiber, so that it will take and hold the dye properly. In kier liming, the lime forms a protective coating on the inside of the iron kier or vat, to prevent staining of the textiles with iron. This process is simply that of applying a lime whitewash and any good lime may be used, but for the other processes in the textile industry a high-calcium lime of more than ordinary purity is required.

New England and northern lime producers in general, like the paper manufacturers, have suffered some losses in recent years because of the shifting of textile mills to the southern states. The probabilities are that the woolen and flax textile industries will in the course of time move nearer to sources of raw material.

War-developed Uses

An important use for magnesium lime came into being during World War II, when a large demand arose for magnesia refractories and for the metal magnesium. Prior to that time, magnesium had been produced in this country only by electrolysis of magnesium brines. During the war, new processes were developed for reducing magnesium oxide by briquetting the lime with ferrosilicon and distilling off the reduced metal in specially designed retorts. A similar process has since been experimented with to produce metallic calcium. A few lime manufacturers became magnesium producers; others sold the lime or the dolomite to the metal producer. Since the war, the slackening demand for magnesium has led to the closing, at least temporarily, of most of these plants.

The demand for domestic magnesia has continued, apparently because of troubles in the Balkans and Greece, where much of the imported magnesite was obtained. In some of the processes developed in the United States, dolomitic lime is used to treat sea water or other brines containing magnesium salts, to precipitate magnesium hydrate, which is subsequently thickened and filtered and serves as a basis for producing magnesia by one of two or three processes. High-calcium lime may be used but in the use of dolomitic or magnesium lime some of the magnesia in the lime is recovered, in addition to that made from the sea water. The magnesia produced is used chiefly in the manufacture of refractories in competition with native and imported magnesite. The market for lime manufacturers is limited to a few producers of magnesia and some of these purchase dolomite and make their own lime.

Another war-developed use for lime is for recovering aluminum from clay. Since the end of the war, it has been found that as long as

bauxite is available the new process probably cannot compete. Limestone was used but the process involved its calcination by the processor of the clay.

PRICE HISTORY

Like any other basic commodity, where the capacity to produce almost always exceeds demand, except for limited periods, the price of lime has fluctuated more from competitive conditions than from changing costs. The element of increasing cost during the past few

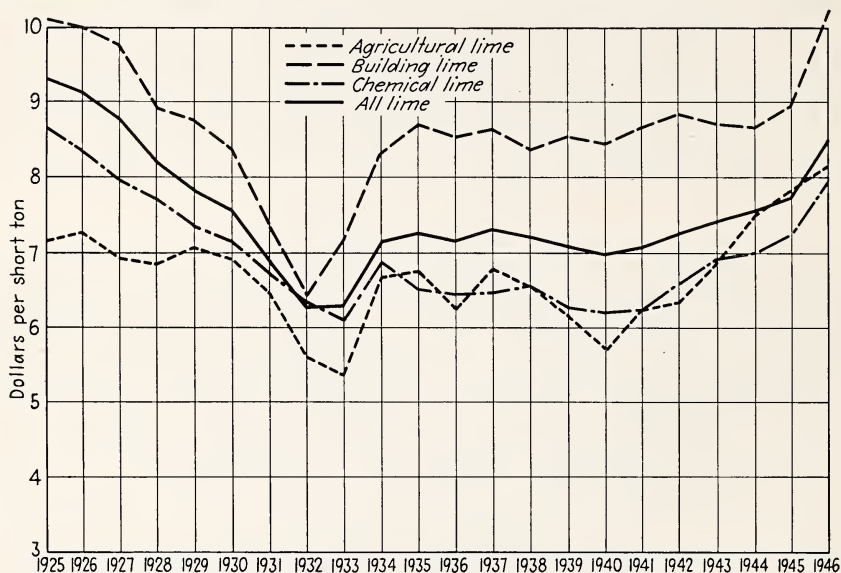


FIG 11—PRICE RANGE OF VARIOUS TYPES OF LIME, 1925-1946.

From statistics compiled by the Bureau of Mines.

years has generally been discounted by more efficient use of fuel and labor, but in periods of slack demand, large producers, in order to keep costs down, through volume production and continuous operation, often resort to price cutting. However, in this respect the industry has become much more stabilized than when competition was chiefly that of a few large producers against many small ones. The small operator had one advantage in that he was able to shut down and start up without the losses entailed to a larger operator, because of the negligible overhead of a small lime plant.

As in the portland cement or other similar industry, the cost of manufacturing lime is influenced more by the volume over which the annual cost is spread than by any other single factor. Overhead costs are constantly increasing because modern lime plants require many times the investment formerly considered ample, technical staffs of higher grade are needed for research and operation, and salesmen must

often be specialists in the particular industries served by the lime manufacturer. On the whole, sales and distribution costs probably are relatively low compared with such industries as portland cement, because no great amount of general advertising is done and the number of customers is not large, especially for chemical and industrial lime.

Net mill prices (or values) per ton of lime, exclusive of the package, are shown in Fig 11. The lower relative prices for agricultural lime reflect the fact mentioned earlier in this chapter, that such lime usually represents a product not pure enough for many chemical uses; and also the fact that it also represents in many cases the product of numerous small operations. The relatively higher prices received for building lime are largely accounted for by the fact that this represents to a considerable extent Ohio finishing lime, which is a premium product for white-coat plaster. The prices of chemical lime are influenced by the fact that much of it is sold on long-term, large orders, often under threatened or actual competition by the consumer industry.

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Recent literature is scattered through many booklets and bulletins of the U. S. Geological Survey, the Bureau of Mines, the Bureau of Standards, the transactions or proceedings of the National Lime Association, the American Society for Testing Materials, the American Chemical Society, the industrial journals of the lime and chemical industries, and scientific journals generally. Most of the state geologists have investigated and reported on the limestone resources and the lime industry of the various states, and some of these state geological reports are splendid sources of information on the uses of lime; such, for example, as those of the states of Pennsylvania, Ohio, and Illinois.

It would be impossible here to give an adequate bibliography on lime, since there are so many phases of the subject that would require extensive research in specialized fields, where lime has been studied for the part it plays in some process. The literature of the production of that particular commodity would have to be searched. For example, the literature of the iron and steel industry contains many technical discussions on the use of lime in metallurgy, and the effect of different limes on the properties of the resulting slag. The literature of the paper-mill industry, particularly the transactions of its technologic associations, contains numerous discussions of the use of lime in that industry. The seeker of detailed and up to date information on the application of lime in modern industry should therefore look into the bibliographies of those industries as well as any bibliography of the lime industry itself.

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CHAPTER 23

LITHIUM MINERALS

By RUSSELL W. MUMFORD*

LITHIA compounds have a place in pharmaceutical and other chemical industries and lithium minerals in glassmaking and ceramics. The metal, although rare, is used to a minor extent in alloys. During the nearly 50 years of production of lithium minerals in the United States, the silicate mineral spodumene has continued as the chief source of raw material for the manufacture of lithium salts. Although twice as much lepidolite, a lithium mica, has been mined, most of it has been used in the making of certain types of glass. Amblygonite has been an additional but minor source of lithium compounds. Triphylite, petalite, and zinnwaldite have also been utilized in the past. All of these commercial lithium minerals contain low percentages of lithium (Table 1).

In 1938, a new raw material for manufacture of lithium compounds made its appearance. This product was crude dilithium sodium phosphate (Li_2NaPO_4), obtained as a by-product of manufacture of potash and soda chemicals from the brine of Searles Lake, California.

Searles Lake, which is now dry, lies in the extreme northwest corner of San Bernardino County, California, and consists of a large mass of salts. It was estimated by the United States Geological Survey that the crystal body contained about 25 pct voids, which are filled with a saturated brine. The brine consists mainly of the sulphates, chlorides, carbonates, and borates of sodium and potassium. Several other acid radicals, including phosphates, are present. Lithium is present in the brine in an amount corresponding to 0.0115 pct Li_2O . In the course of evaporation of water from the brine, during the process of manufacture of sodium and potassium chemicals, dilithium sodium phosphate crystallizes out and is recovered by a flotation operation. The lithium concentrate is filtered and dried and is then ready for shipment. It analyzes from 19 to 21 pct Li_2O and now constitutes the highest known grade of crude lithium material. It is and will continue to be a major source of lithium for manufacture of lithium products.

The variation in lithia content of the commercial minerals as mined is due to replacement of the lithia by soda and potash, to partial alter-

* Vice President and Consulting Engineer, American Potash and Chemical Corporation, Los Angeles, California.

ation of the mineral to nonlithium minerals, and to the presence of impurities.

TABLE 1—*Composition of Commercial Lithium Minerals*

Mineral	Simplified Formulas	Theoretical Content, Pct		Range in Commercial Mineral, Pct
		Lithium (Li)	Lithia (Li ₂ O)	Lithia (Li ₂ O)
Spodumene....	LiAlSi ₂ O ₆ or Li ₂ O.Al ₂ O ₃ .4SiO ₂	3.73	8.03	4-8
Lepidolite.....	LiKAlF ₂ Si ₃ O ₉ or LiF.KF.Al ₂ O ₃ .3SiO ₂	1.90	4.09	2-4
Amblygonite....	LiAlFPO ₄ or 2LiF.Al ₂ O ₃ .P ₂ O ₅	4.69	10.10	8-9
Triphylite.....	LiFePO ₄ or Li ₂ O.2FeO.P ₂ O ₅	4.40	9.47	2-6
Petalite.....	LiAlSi ₄ O ₁₀ or Li ₂ O.Al ₂ O ₃ .8SiO ₂	2.27	4.89	2-4
Zinnwaldite....	LiKFeAl ₂ F ₂ Si ₃ O ₁₀ or LiF.KF.FeO.Al ₂ O ₃ .3SiO ₂	1.58	3.40	2-3

Spodumene occurs in distinct, prismatic, characteristically large crystals with a nearly square, rounded, or flat cross section. In South Dakota, crystals 20 to 30 ft long are numerous—one measured 47 ft. A diameter of 3 to 4 ft is not rare. The commercial mineral is dull gray-white. Transparent colored varieties, such as triphane (yellow), hiddenite (green), kunzite (purple), are used as gems. The hardness of the fresh mineral is 6.5 to 7, its specific gravity is about 3.17. Spodumene is monoclinic and has the crystal habit of pyroxene, the prismatic cleavage angle being 93°. It fuses easily before the blowpipe flame, which it colors crimson, as do all the other lithium minerals.

Lepidolite commonly forms compact aggregates of glittering scales, only a fraction of an inch across, with a characteristic pink or purple tint. It may also be white, gray, yellow, purple, or blue. Its hardness is about 3, and specific gravity about 2.85, with perfect micaceous cleavage. Zinnwaldite is similar in properties except for color, which is brown, yellow, violet, or dark gray.

Amblygonite is generally massive, showing imperfect cleavage faces. It is white and resembles some white feldspar, though its specific gravity (about 3.1) is higher. Its hardness is 6. Triphylite is found in cleavable masses, gray or brown, commonly stained black by separated manganese oxide, as all triphylites contain some manganese. Its hardness is 5 and specific gravity 3.5. Petalite usually is massive, resembling amblygonite and spodumene, and is white or gray.

All the lithium minerals are typical constituents of granitic pegmatites. Zinnwaldite occurs also in veins and greisens. Most of the occurrences show evidence that they have been introduced into already formed pegmatites by hydrothermal solutions replacing earlier feldspars.

In general, they occupy a somewhat central position in the pegmatites, of which they may constitute a large portion.

DISTRIBUTION OF DEPOSITS

Much of the spodumene commercially produced in the United States has come from the Black Hills of South Dakota, chiefly from the Etta mine near Keystone, Pennington County, and the Tin Mountain mine near Custer, Custer County. In 1944, a substantial quantity of spodumene was produced by Black Hills Tin Co. at Tinton, South Dakota. However, spodumene is abundant in many of the pegmatites of that region and has been produced from many other mines than those mentioned. Similarly, amblygonite is widespread in its occurrence in the region and has been mined together with the spodumene and much smaller quantities of triphylite and lepidolite. The area enclosing Keystone, Custer, and Pringle would roughly outline this lithium province. The Black Hills region of South Dakota probably will continue to be a major source of lithium minerals in the future, as it has been in the past.

The Stewart mine, at Pala, San Diego County, California, has produced large quantities of lepidolite and smaller quantities of amblygonite. Active production ceased some time ago. Similarly, the Harding mine, 13 miles east of Embudo, in northern New Mexico, produced considerable lepidolite for a time but has not been very active in recent years. In 1939, lepidolite was produced from the Ingersoll mine, by the Black Hills Keystone Corporation. Substantial reserves of spodumene are reported developed in the Edison mine, near Keystone. Spodumene is said to have been mined and shipped recently from a pegmatite mass near Warren Station, Knox County, Maine, about 60 miles northeast of Portland. In the past, small quantities of spodumene and lepidolite were produced in Maine, Massachusetts, and Connecticut. Other deposits have a potential value, although little is known of the quantity of lithium minerals present. Probably the most important of these is the group of pegmatites extending through the town of Kings Mountain, Cleveland County, North Carolina. Here certain zones are said to average about 20 pct of spodumene for considerable distances. Following development of a flotation process, the Kings Mountain deposit was a large producer of concentrated spodumene during the period May 1943 to February 1945.

In Colorado, several thousand tons of lepidolite is estimated to occur in Gunnison County, 2 miles southwest of Ohio City. In Fremont County, a few miles west of Canon City, lepidolite and amblygonite were found. Specimens of lepidolite, amblygonite, and petalite have been obtained in Fremont County, Wyoming. The extent of these undeveloped deposits in Colorado and Wyoming is not known.

One of the most important known deposits of lithium minerals outside of the United States is in southeastern Manitoba, Canada (spodumene, amblygonite and lepidolite). Other important foreign occurrences include Utö, Sweden (petalite, lepidolite and spodumene); the Erzegebirge between Saxony, Germany, and Bohemia, Czechoslovakia (zinnwaldite); Mount Hradisko, near Rozna, Moravia, Czechoslovakia (lepidolite); Montebbras and neighboring places in Creuze Department, France (amblygonite and lepidolite); the San Finx mine near Silleda, Pontevedra district, Galicia, in northwestern Spain (amblygonite); Caceres, Caceres district, Estremadura, in southwestern Spain (amblygonite); near Guarda, Portugal (amblygonite and lepidolite); Central Damaraland, Southwest Africa, said to be capable of furnishing from 50,000 to 60,000 short tons of lepidolite, running at least 4 pct Li_2O ; and Western Australia, where amblygonite, spodumene and lepidolite are reported to occur in sufficient abundance to supply the world market.

Deposits of lithium minerals in the United States could yield considerably increased production should occasion arise. The United States has produced the great bulk of lithium minerals mined and consumed, although with increased demand the deposits in Canada, Western Australia, and Southwest Africa may become important producers. The United States has both imported and exported small quantities of crude lithium minerals. There is a tariff of 25 pct ad valorem on metallic lithium and lithium salts.

PRODUCTION AND MARKETING

The production of lithium minerals has always been an insignificant part of the total mineral production of any country. Domestic production of spodumene began in South Dakota about 1898 and has continued ever since, with a total quantity of about 22,000 tons at the end of 1935. Amblygonite has been mined continuously there since about 1910, with a total of slightly more than 4000 tons. The total production of lepidolite, together with a very small quantity of amblygonite from the Stewart mine at Pala, California, is about 24,500 tons. The Harding mine, New Mexico, became an active producer of lepidolite at about the time the California deposit ceased to be an important source and has produced about 19,000 tons.

The sharp upturn during the years 1942 to 1944 in production of lithium ores and compounds in the United States is clearly shown in Table 2. This increase in output was caused by demands for lithium products engendered by war activities.

Mining methods are very simple. The crystals (as of spodumene) or masses (as of lepidolite and amblygonite) are hand-picked from the broken pegmatite rock. Most of the lepidolite mined and much of the amblygonite occurs in solid masses many feet thick, which are simply

TABLE 2—*Shipments of Lithium Ores and Compounds from Mines in the United States*

Year	Short Tons	Value	Tons Li ₂ O
1935-39 avg	1,327	\$ 48,280	88
1940	2,011	80,679	113
1941	3,832	115,718	209
1942	5,405	243,516	299
1943	8,155	314,660	463
1944	13,319	552,977	848
1945	2,446	285,520	274
1946	3,065	303,892	323
1947	2,441	151,113	199

broken down to a size convenient for handling and shipping. The crystals of spodumene from South Dakota are so immense that single crystals yield many tons of material suitable for shipment.

No unusual preparation is required before shipment, although pieces of lepidolite containing much quartz and feldspar must be rejected. Where the mineral is to be used directly, as in manufacture of glass, all iron minerals must be removed. The lepidolite from New Mexico was unusually low in iron, containing only a few hundredths of one per cent. Where the spodumene is covered with a soft, claylike material (as in South Dakota), this must be broken off, because it contains almost no lithium.

During 1938 and 1939, a process was developed by the United States Bureau of Mines in cooperation with the Tennessee Mineral Products Corporation for beneficiation of the spodumene deposits at Kings Mountain, North Carolina. A commercial flotation plant was constructed and operated from 1943 to 1945, and during 1944 was the largest producer of spodumene in the United States. The Black Hills Tin Co., at Tinton, South Dakota, perfected a flotation process for separating spodumene from quartz. During 1944, a plant using this process was the second largest producer of spodumene in this country. The concentrates produced by these flotation processes averaged about 6 pct Li₂O.

A minimum content of lithia approximating the lower figures in the percentage range for the commercial minerals is usually specified. A price may be fixed with a bonus for lithia content exceeding the fixed minimum. For use in glass and ceramic industry, the iron content must be very low.

The following nominal prices were quoted for lithium ores in 1947:

- Spodumene, 6 pct Li₂O minimum, \$6 to \$8 per unit
- Amblygonite, 8 to 9 pct Li₂O, \$42 to \$50 per short ton f.o.b. mine
- Amblygonite, air-floated, \$110 per ton in carlots
- Lepidolite, 3 pct Li₂O, \$24 to \$25 per short ton f.o.b. mine
- Lepidolite, 4 pct Li₂O, lump, \$56 per ton; powdered, \$80 per short ton

Crude dilithium sodium phosphate is reported to sell in carlots in bags at a price of \$9 per unit of Li_2O .

Lithium metal, 98 to 99 pct, is quoted at \$15 per pound f.o.b. New York.

USES

The earlier use of lithium minerals was almost entirely as source material for the preparation of lithium compounds. About 20 to 25 years ago, use began of lepidolite directly as an ingredient in glass-making. Recently, renewed interest has been shown in the direct use of both spodumene and lepidolite in the glass and ceramic industries. Lepidolite is a very good fluxing material. It also decreases the coefficient of expansion and increases the strength of glass, glazes, enamels, and porcelains. Its content of lithia and fluorine, high total alkali and alumina, moderate silica and very low iron, are beneficial. The lithia makes the glass more durable and is of advantage where high electrical resistance is desired. In larger quantities, lepidolite is a good opacifier and has been used in making opal or white opaque table tops, translucent white glass for indirect lighting fixtures, ointment jars, and tops of fruit jars. Amblygonite used directly seems also to be beneficial in ceramics and is reported to have been so used in glass and porcelains in France. Spodumene also is said to improve the quality of certain ceramic wares.

Minute quantities of metallic lithium impart valuable properties to certain metals (aluminum, lead, magnesium, zinc) and alloys, increasing their hardness, toughness and tensile strength. Bearing-metal alloys, copper electrodes, and lead cable sheaths are so benefited. In the higher-melting metals and alloys, such as iron, nickel and copper, lithium acts as a degasifier, deoxidizer, desulphurizer, and general purifying agent. The lithium is generally introduced as a calcium-lithium alloy.

Manufactured salts of lithium have been put to many uses, perhaps the most widely recognized of which is in the pharmaceutical trade, large quantities being used in the preparation of mineral waters and lithia tablets. Alkaline storage batteries, using lithium hydroxide, formerly consumed large quantities. In other uses the quantity consumed for any one item may not be large but in the aggregate amounts to an appreciable figure. The chloride and fluoride are used in welding fluxes, especially for aluminum; the borate in dental cement; the nitrite for curing meat; the hydroxide for mercerizing sulphite cellulose for rayon and for purifying helium and other rare gases. Among many other uses of lithium salts may be mentioned that of producing red color in flares and fireworks.

A recent use of lithium chloride and lithium bromide that may

become extensive in the future is for dehumidifying air for air conditioning and industrial drying.

The wartime need for lithium arose in part from its use in radio and fluorescent light tubes, optical lenses, greases to counter extremes of heat and cold, and as a carrier of hydrogen in the form of lithium hydride to inflate life-raft radio-antennae balloons.

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CHAPTER 24

MAGNESITE AND RELATED MINERALS

BY RAYMOND E. BIRCH* AND OSCAR M. WICKEN†

THE mineral magnesite, formerly the source of nearly all magnesia, now shares this role with brucite, dolomite, and the world's natural and artificial brines. The mineral magnesite is the normal carbonate of magnesium, MgCO_3 , composed when pure of 47.6 pct MgO and 52.4 pct CO_2 . It is one of the calcite (CaCO_3) group of rhombohedral carbonates, which also includes dolomite, $\text{CaCO}_3\cdot\text{MgCO}_3$, and siderite, FeCO_3 . Magnesite does not form an isomorphous series with calcite or dolomite; consequently, these lime-bearing carbonates commonly present in magnesite deposits are there only as mechanical mixtures. Magnesite and iron carbonates form a continuous isomorphous series and therefore are inseparable mechanically. The variety of magnesite known as breunnerite is an isomorphous mixture of iron and magnesium carbonates.

Magnesite may be either crystalline or amorphous (cryptocrystalline). The former, which includes breunnerite, is often termed spathic magnesite. Crystalline magnesite varies from finely to coarsely crystalline in texture and has a hardness of 3.5 to 4. The color is white, yellowish, blue-gray to drab, red, pink, black, or mottled. It is seldom found pure but usually contains variable amounts of iron, lime, silica, and sometimes manganese. The color cannot be used as an index of purity.

The cryptocrystalline variety is perhaps the more common type but the crystalline variety usually occurs in larger deposits. The amorphous type is fine grained and compact, showing no cleavage. It is usually snow white but sometimes is light to pale orange yellow or buff, owing to impurities. The fracture is conchoidal to uneven and the hardness 3.5 to 5. Silica may be present as inclusions of serpentine, quartz, chalcedony, or other minerals. The lime and iron contents are usually low. In general, amorphous magnesite is somewhat purer than the crystalline variety.

The specific gravity of cryptocrystalline magnesite is 2.90 to 3.00. Pure crystalline magnesite has shown a specific gravity of 3.02 but iron

* Harbison-Walker Refractories Co., Pittsburgh, Pennsylvania.

† Northwest Magnesite Co., Pittsburgh, Pennsylvania.

carbonate, commonly present, raises the specific gravity; typical figures for breunnerite are 3.08 to 3.13.

Magnesite dissociates on heating, by the release of carbon dioxide. The product is magnesia (MgO), which develops, either simultaneously or upon further heating, a crystalline structure and is then known as periclase. The mineral periclase occurs in nature but is rather rare and is not found in workable deposits. When dead-burned or sintered, magnesium oxide is resistant to hydration and carbonation at the temperature and pressure of the atmosphere.

NOMENCLATURE OF PRODUCTS

Magnesite actually refers only to the mineral MgCO_3 , but common usage applies it to most of the manufactured products with a classifying prefatory word; e.g., dead-burned magnesite and caustic magnesite. For the most part, these products are actually magnesia (MgO) and the universal use of this term has been urged by some. However, when magnesia from sea water and brines made its appearance in the world's markets described as "magnesite," the last opportunity to dislodge the older terms became a lost cause.

Dead-burned Magnesite is the granular product obtained by calcining magnesite, or other substances convertible to magnesia upon heating, above 1450°C long enough to form dense, weather-stable granules suitable for use as a refractory or in refractory products (ASTM definition).

Caustic Magnesite is the product obtained by calcining magnesite, or other substances convertible to magnesia upon heating, at a temperature not exceeding 1200°C . From 0.5 to 7 pct ignition loss is shown by the product, depending upon the desired degree of reactivity. Generally, the lower the ignition loss, the lower the reactivity.

ORIGIN,⁶ OCCURRENCE, AND DISTRIBUTION OF DEPOSITS^{13,17}

The crystalline magnesite is generally formed by the alteration of dolomite by magnesian solutions associated with intrusions. The cryptocrystalline variety is an alteration product of serpentine or allied magnesian rocks. It is common in serpentine areas and occurs in fissures or crush zones mixed with serpentine and some opal or chalcedony, also produced by the breakdown of the serpentine. This type of magnesite generally occurs in small deposits, as in the California coast ranges and on the Grecian island of Euboea.

The largest deposits of crystalline magnesite in the United States are those near Chewelah, Washington, and near Gabbs, Nevada. They represent replacements of dolomite under the influence of later intrusives. Probably the largest deposits in the world (also crystalline) are

those at Veitsch, in Styria, Austria, and in Manchuria near Niehsinshan. The Austrian deposit is a replacement of dolomite formed following the intrusion of porphyry and other acidic and basic rocks.

In the United States, magnesite has been mined in Washington and California for many years but resources in the latter state are running out. During World War II, small-scale production began in Texas and large-scale operations in Nevada. In late 1947, mining had ceased at least temporarily in California and the producers of that state were relying on crude magnesite shipped from Nevada to be burned in California to supplement the much greater tonnages of magnesite produced from sea water and bitterns.

In Canada, a large deposit of crystalline magnesite occurs in British Columbia⁷ but the only deposit being worked is that associated with dolomite in the Grenville district of Quebec.

For a single year, 1944, Nevada was reported to be the leading producer of magnesite. The Government-owned plant operated by Basic Magnesium Inc. and later by Anaconda Copper Co. near Gabbs, Nevada, mined, concentrated and calcined rock (in shelf roasters) to be trucked 350 miles to the magnesium-metal plant at Las Vegas. When the latter plant, which required 300 tons daily of caustic magnesite, ceased operation, sufficient ore had been developed to operate the concentrator at full capacity for 10 years.

Viewed as to their long-time influence on the world magnesite industry, the most important deposits have been those of central Europe. This magnesite is of the crystalline breunnerite type and was formed by the replacement of limestone by the action of ascending aqueous solutions carrying magnesium and iron compounds. Of the many deposits of this type that exist in a belt through central Europe, about a dozen are large enough to be workable. The narrow belt in which they occur extends westward from Semmering, Austria, the most important occurrences being at Semmering, Veitsch, Brietenau, Trieben, Radenthein, and Dienten. The deposits are lenses; of which by far the most celebrated and most important is the one at Veitsch, near Mitterndorf in Styria, Austria (its reserves were estimated at 50 years in 1946). The magnesite lens at Radenthein (estimated proved reserves, 20 years) is also of considerable extent. Although this belt comprises the major part of the workable deposits of central Europe, Yugoslavia and Czechoslovakia also are producers.²⁰

The USSR was the world's leading producer of magnesite before World War II. The U. S. Bureau of Mines reported USSR average annual production of crude magnesite for the five years prior to 1939 as 535,000 tons. Comparative data in thousands of tons were 403 for Austria, 233 for Manchuria, 157 for the United States, 134 for Greece, and

83 for Czechoslovakia. Dead-burned magnesite from Manchuria first entered the United States markets in 1936, and by 1941 accounted for 91 pct of all importations.

Greece and British India are the only important producing countries whose major output is derived from cryptocrystalline magnesite. In British India, most of the production is from the Salem district, in the Madras Presidency, but some supplies come from Mysore. Magnesite exportations from Greece began in 1870 and that country continued to hold an important world position in the industry until World War II. A peak production was reached in 1916 at about 200,000 tons (crude rock).

Deposits large enough to have a bearing upon the future of the industry occur also in Korea, Brazil, and Argentina. Australian supplies are adequate for her own needs.

PROSPECTING AND EXPLORATION

The conjunction of dolomitic or calcareous areas with one of igneous activity, or an area wherein serpentinization is abundant, are possible locations of the various magnesites. Magnesitic formations are generally more resistant to weathering than associated formations, and consequently bold outcrops characterize magnesite deposits. Newly discovered outcrops are sampled by surface chipping and by shallow trenching. Field differentiation between magnesite of commercial purity and magnesite containing excessive lime can be aided by the use of cold dilute hydrochloric acid. Calcite will effervesce under hydrochloric acid whereas magnesite will not. After a preliminary idea of the size and quality of the deposit has been obtained, diamond drilling is employed to further delineate the ore body, particularly in massive deposits. The evaluation of magnesite deposits is based on the amount of silica, lime, and alumina contained, and on the degree of dispersion of these impurities. Generally, to be of grade acceptable to the refractories industry, the magnesite prior to dead-burning must contain at least 90 pct magnesium carbonate.

MINING AND PROCESSING

The mode of mining is dependent upon the type of deposit. Massive deposits are generally worked by modified open-pit quarry methods; others are worked both by narrow surface openings and by underground drifting and stoping.

Washington

Washington magnesite occurs as massive replacements in dolomite. Haphazardly distributed throughout the magnesite are stringers and lenses of siliceous and calcareous impurities. The magnesite deposits are found in several places along the formation known as the Stensgar

dolomite. Although magnesite outcroppings are numerous in this formation, only a few are being exploited. These are the Finch, Allen-Moss, Keystone, and Red Marble quarries. The Finch and Allen-Moss were the original quarries of the Northwest Magnesite Co. and until 1945 all of the production came from those two operations. In 1946, the Keystone deposit was brought into production after extensive diamond drilling had outlined the ore body. Prior to the actual mining at the Keystone, a large cap of dolomite was removed in order that the Finch and Allen-Moss quarry methods could be used. At the present time (1948) the Red Marble deposit is being developed. It will be brought into production in 1949.

In all cases the mining operations are similar: 20 to 30-ft levels are opened up and advanced in a series of working faces, which may be just wide enough to allow the operation of a power shovel or many times as wide. Drilling for primary rock breakage is accomplished by putting down vertical wagon drill holes from the bench above a given working level. Some secondary jackhammering and plugging is necessary to reduce the rock to sizes that can be handled by power shovels. The broken ore is loaded into trucks, which discharge into oreways. Much of the Finch rock is trucked directly to the mill.

At the Finch and Allen-Moss quarries, the magnesite is withdrawn from the oreways into a train of underground cars and is transported 1000 to 2000 ft to the milling plant. At the Keystone operation, all oreways feed into one gathering oreway, which in turn discharges into an underground jaw crusher. The crushed rock is conveyed by belt several hundred feet underground and then discharged into a surface bin, which loads directly into aerial tramway buckets. The tramway delivers the ore to the milling plant near the Finch quarry, 4 miles away.

Rough separation of ore and waste such as is possible with a power shovel is made at the quarry faces. Prior to 1943, most of the ore was hand-sorted but since the completion of the heavy-media concentrating plant, all hand sorting has been eliminated.

Crude ore is treated as follows: The ore is brought from the various operations by aerial tramway, mine cars and conveyor belts, to a coarse-ore bin, or, for the Keystone ore, to the middling-ore bin. The ore is crushed by means of jaw and gyratory crushers, washed and screened by means of rotary scrubbers and vibrating screens, and the $-1\frac{1}{2} + \frac{1}{8}$ -in. fraction is discharged into the heavy-media cone feed bin. The minus $\frac{1}{8}$ -in. sands are stock-piled for future treatment. The sized ore from the cone feed bin is beneficiated in a 20-ft diameter heavy-media cone. The floats, or waste, consisting of dolomite, quartz, and other undesirables, are rejected to a tailings pile, and the sinks, or magnesite, are crushed by gyratory and roll crushers to pass a fine screen in closed cir-

cuit with the crusher. Most of the crushed magnesite is then transported 5 miles by aerial tramway to the calcining plant, where it is blended with iron ore and dead-burned at about 2900°F in six rotary kilns, to produce "standard" dead-burned grains. Five of the kilns are 7 ft 6 in. by 125 ft long. The sixth kiln is 9 ft 6 in. by 8 ft 6 in. in diameter by 306 ft long. The large kiln has 10 forward flow coolers. The small kilns have separate rotary aftercoolers. The standard grains are crushed and screened to yield a variety of sizes for different refractory applications.

The magnesite that is not directly transported to the calcining plant is conveyed by conveyor belt to a flotation mill for further beneficiation. Some of the minus $\frac{1}{8}$ -in. screenings from the heavy-media mill are also treated in the flotation mill. The fine magnesite is further reduced to minus 65-mesh size by a ball mill in closed circuit with a classifier. Pure magnesite is floated away from impurities. The magnesite concentrate is thickened, filtered, dried in a rotary drier and transported to the calcining plant by aerial tramway. At the calcining plant, the concentrates are dead-burned in an 8-ft 6-in. by 125-ft rotary kiln. This high-grade burned magnesite is cooled and stored in bins for shipment to eastern brickmaking centers.

California

California magnesite has been reported in many places throughout the state. However, very few of the deposits are of commercial size. The magnesite is cryptocrystalline or amorphous material derived from the alteration of serpentine. Although deposits may have many stringers and lenses of impurities, the magnesite itself is very pure.

Magnesite mined in California has been produced by several companies during the past several years. However, the mining of magnesite in this state has long since passed its peak and at present, according to M. Y. Seaton, Executive Vice President, Westvaco Chemical Division of Food Machinery and Chemical Corporation (private communication), no mines are operating in virgin ore. The Westvaco Chemical Division is engaged currently in working over a deposit of stock-piled ore at its Western mine.

The only present milling operation in California involving natural magnesite is that of the Westvaco Chemical Division. The stock-piled ore from the old Western mine is crushed and screened. Because the impurities other than lime are softer than the magnesite, a concentration of silica, alumina, and iron impurities tends to appear in the minus $\frac{1}{8}$ -in. fraction, which is rejected. The coarse magnesite is transported to Newark, California, for processing. All of this production is devoted to caustic magnesite.

Nevada

The magnesite industry in Nevada centers about 35 miles from Luning, at Gabbs, Nye County. The magnesite occurs as a replacement in dolomite. The deposits are similar to those in Washington in that both were formed by the action of igneous intrusives on the dolomitic formations. The individual deposits are smaller than those in Washington. The magnesite is similar to Washington magnesite in chemical analysis and appearance. The hydroxide, brucite, is found in substantial quantities throughout the formation in addition to the carbonate.

This area was the scene of the large-scale Defense Plant Corporation plant operated by Basic Magnesium, Inc. For a time this operation, which has been well described in the literature,^{2,16,18} was the largest single producer of calcined magnesia in the country. All of its production was consumed in the manufacture of metallic magnesium. The operation of this plant was terminated in October 1944. At present only the privately owned Sierra Magnesite and Basic Refractories deposits are being operated.

Westvaco Chemical Division together with Permanente Metals Corporation jointly own the Sierra Magnesite Co., which operates a quarry at Gabbs. They have been mining and shipping magnesite to the Pacific Coast since 1940.² Some of the crude ore is removed by open-pit methods from benches 20 to 30 ft high. Working faces are generally narrow because of small horizontal dimensions of individual pockets of magnesite. Generally dikes and intrusions of gangue are removed prior to ore breakage at any given face. Then, when the ore is shot down, it can be removed with a minimum of contamination. The broken ore is discharged through oreways to underground conveyor-belt haulage to the surface. Currently a large part of the production is also being mined by underground methods. All the crude ore is crushed and screened prior to shipment to the two companies' California processing centers.¹⁹

Near the Sierra Magnesite deposit is a deposit of ore consisting largely of brucite, owned and operated by the Basic Refractories Co., of Cleveland, Ohio. The mining of the deposit has been continuous since 1935. Open-pit benching is the method used. After the ore is shot down, the high-grade portion is selected for shipment to Ohio and the low-grade portion is stock-piled for future treatment.

Quebec

A deposit of high-lime magnesite is being mined by the Canadian Refractories, Ltd., at Kilmar, Quebec, about 70 miles northwest of Montreal.⁸ The magnesite occurs as a series of veins up to 30 ft wide.

The veins dip about 85° from the horizontal and have a footwall of quartz monzonite and a hanging wall of serpentine, diopside, and quartzite.

From 1915 to 1936, the mine was operated by narrow, deep, open-cuts. Since 1936, the mine has been operated by underground methods. Shafts are sunk to the desired level and drifts and crosscuts are driven into the veins. The ore is then removed by shrinkage stoping. Chutes discharge into cars, which are individually hoisted to the surface in a cage.

The ore discharged from the cars is crushed to 5-in. size, washed, and hand-sorted on a picking conveyor. The magnesite is then carried by locomotive haulage about a mile to the calcining plant, where large portions are stock-piled to obtain uniform blending. Material withdrawn from this pile furnishes feed for the crushing operation. The crushed magnesite is ground dry in a ball mill to provide fine feed for the rotary kilns. Prior to 1947, all dead-burning was done in three 65-ft kilns. Now, however, a 9 by 220-ft kiln is used. Early in 1949, a heavy-media plant was put into operation in order to obtain closer control over the quality of the magnesite produced.

The Aluminum Company of Canada is mining a unique deposit of brucite at Wakefield, Quebec.¹¹ This brucite occurs as rough grains $\frac{1}{16}$ to $\frac{1}{8}$ in. in diameter, disseminated through a limestone matrix. The brucite content is about 29 pct of the weight of the rock. The ore is removed by power shovel and trucks from three or four 25 to 30-ft benches. The trucks haul the ore directly to an apron feeder ahead of the primary crusher.

The ore is crushed and screened to provide several closely sized fractions for use as kiln feed. Two rotary kilns are used to calcine the brucitic limestone. Adequate reactivity of the limestone is assured by very careful control of the calcining operation. After calcination, the lime is crushed, screened, and slaked in a dry hydrator. The entire operation is controlled so that the discharge from the slaker consists of an impalpable dust of hydrated lime mixed with granules of magnesia: An air separator is used to separate the two products, after which the granules are washed in a wet classifier. When this product is to be used for refractory purposes, it is dead-burned at the Kilmar plant of Canadian Refractories, Ltd.

SYNTHETIC MAGNESITE

During the past decade the manufacture of dead-burned and caustic magnesias from material sources other than natural magnesite or brucite has become increasingly important. In all but one of the commercial plants making synthetic magnesias, the basic reactions are alike. These reactions are the calcination or dead-burning of magnesium

hydroxide obtained by precipitating it from magnesium salt solutions such as sea water, sea-water bitterns, or inland brines, by means of calcium hydroxide derived from oyster shells, limestone, or dolomite. For the precipitation of magnesium hydroxide, any of the magnesium salt solutions can be used with any of the sources of calcium hydroxide. The main consideration in establishing the choice of reactants is purely an economic one, depending on proximity of suitable raw materials. After the reactants are established for any given plant, however, the limitations of pumping and thickening equipment will prevent that plant from changing to reactants more dilute than those for which the plant was designed; that is, a plant using sea-water bitterns cannot change to the use of raw sea water, nor can one using dolomite change to one using limestone without sacrifice of production. However, the reverse changes would be entirely feasible.

The size and capacity of equipment to handle and calcine limestone, oyster shells, and dolomite is about the same per unit of magnesia in all plants making synthetic magnesia. The same is true of operations pertaining to the calcination or dead-burning of magnesium hydroxide. However, the size of equipment to handle the magnesium salt solutions and the precipitated magnesium hydroxide varies considerably, depending on the choice of reactants. Plants using sea water and limestone or oyster shells require large sea-water softening systems and large thickening capacity for the precipitated magnesium hydroxide. Plants using sea water and dolomite require one half as much capacity for the sea-water softening and magnesium hydroxide-thickening equipment. This follows from the fact that in plants using dolomite the magnesium salt solution provides only half the magnesia. Plants using concentrated brines or bitterns require no softening equipment and relatively small thickening equipment, depending on the volume of liquid, which in turn depends on the concentration of magnesium salts. These last plants, however, sometimes require pretreatment of the brines in order to remove sulphates or other impurities.

The production of precipitated magnesium hydroxide from sea water dates back to the end of the last century, when a small operation existed for a short time on the Mediterranean coast of France.⁹ The Marine Magnesium Products Corporation, the first commercial producer in this country, makes a variety of magnesium compounds in its plant at South San Francisco.¹ The raw materials are sea water and calcined limestone or dolomite. Analysis of the sea water, in grams per liter, is:¹⁴

NaCl	27.319	CaSO ₄	1.268	R ₂ O ₃	0.022
MgCl ₂	4.176	Ca(HCO ₃) ₂	0.178	SiO ₂	0.0076
MgSO ₄	1.668	K ₂ SO ₄	0.869	B ₂ O ₃	0.0215
MgBr ₂	0.076				

This sea water is more dilute than that of the open ocean. The calcined limestone is exceptionally pure and probably contains less than 2 pct total impurities.

The sea water entering the plant is chlorinated, to remove organic material, and then treated with a small amount of slaked lime, to precipitate bicarbonates as carbonates. After a thickening operation that removes most of the insoluble impurities, the treated sea water is filtered by sand filters to yield a clean, softened solution. In the softening operation, enough slaked lime is added to precipitate a small part of the magnesium ions as magnesium hydroxide. This makes for a more voluminous precipitate, which helps to sweep out the silica and carbonates.

The softened and clarified liquid is then combined with enough slaked lime to precipitate most of the remaining magnesium ions as magnesium hydroxide. The slurry of magnesium hydroxide and spent sea water is thickened and washed to yield a pure magnesium hydroxide. The magnesium hydroxide is used as a raw material for the preparation of a multitude of different magnesium compounds. All of the production of this plant is consumed in the specialty markets requiring very pure materials.

Three other plants using raw sea water are those of the Permanente Metals Corporation at Moss Landing, California; the Northwest Magnesite Co., at Cape May, New Jersey, and the Dow Chemical Co., at Freeport, Texas. This last plant uses calcined oyster shells as the precipitant but the other two use calcined dolomite. Some differences, such as direct addition of calcined dolomite to the softened sea water instead of preliminary slaking, exist among these plants, but essentially they operate on the same principles as the other plants described.

One synthetic-magnesite plant, Westvaco Chemical Division at Newark, California, is steadily producing caustic and dead-burned magnesite from sea-water bitterns and dolomite. Until recently, oyster shells dredged out of San Francisco Bay furnished the calcium hydroxide used as the precipitant but now the company has a source of excellent dolomite, which it began to use in 1943.

The analysis of the bitterns, which are a by-product from a local saltmaking operation, falls in the following range:¹⁹ NaCl, 12.5 to 16.0 pct; $MgCl_2$, 6.0 to 8.7; $MgSO_4$, 4.2 to 6.1; KCl, 1.4 to 1.9; $MgBr_2$, 0.14 to 0.20. No removal of carbonate is necessary but sulphate must be removed before the precipitation of magnesium hydroxide or else the product will contain large quantities of calcium sulphate. The removal of sulphate is accomplished by combining the bitterns with calcium chloride from another step in the operation. The gypsum thus precipitated is dried and sold. Part of the sulphate-free bittern is added to all the finely ground calcined dolomite in the first compartment of a two-

stage combined slaker and reactor. After this mixture leaves the first compartment and enters the second, it is combined with the remainder of the bittern. The reaction, partially completed, is continued to completion in secondary reaction vessels under conditions of mild agitation. The product obtained is a semirigid, spongelike structure that thickens and filters speedily.

The completely reacted slurry from the last reaction vessel is washed with softened fresh water in a series of five 55-ft thickeners. The underflow from the last thickener, containing about 2.2 lb $\text{Mg}(\text{OH})_2$ per gallon, is sent either directly to rotary vacuum filters or to batching tanks for adjustment of composition by adding certain materials, and then to filters. In either event, the filter cake is fed into rotary kilns for the production of dead-burned magnesite and caustic calcined magnesite. The dead-burning kiln has a feed end diameter of 11 ft, a discharge end diameter of 7 ft, and a length of 190 ft. The two caustic calcining kilns are about 6 ft in diameter. One of them is 80 ft long and the other is 100 ft long.

The calcining operations are carried out at a variety of temperatures, in order to produce magnesias of different degrees of activities for different uses. The dead-burning operation is carried out at temperatures in excess of 3400°F , which is higher than those met with in similar commercial operations.

The final products are cooled, crushed, and screened if necessary, and shipped to consumers.

Three magnesia producers—the Dow Chemical Co., at Ludington, Michigan; the Michigan Chemical Corporation, at St. Louis, Michigan, and the Standard Lime and Stone Co., at Manistee, Michigan—use well brines and calcined dolomite to precipitate magnesium hydroxide, which is calcined to yield caustic calcined or dead-burned magnesite. A typical analysis of the brine is as follows: NaCl , 5.8 pct; CaCl_2 , 17.0; MgCl_2 , 9.9; KCl , 2.5; Br , 0.1; sp gr, 1.29; pH, 5 ± 0.5 .

The brine is pumped to the surface from depths of 2500 to 3500 ft. Removal of sulphates or bicarbonates prior to precipitation of the magnesium hydroxide is not necessary. Aside from the omission of this step, the processes parallel, with minor differences, the process used by Westvaco. Certain of these plants make only caustic magnesite but others manufacture both the caustic and dead-burned products.

The foregoing processes have been based on the reaction between a soluble magnesium salt and calcium hydroxide to produce magnesium hydroxide. A somewhat different process is used by the Diamond Alkali Co. at Painesville, Ohio,⁴ where production of dead-burned magnesite was begun in 1948. By substituting calcined dolomite for calcined limestone in the Solvay process for making soda ash, the spent material from the ammonia stills consists of a slurry of magnesium hydroxide in a solu-

tion of calcium chloride instead of calcium chloride alone.⁵ The slurry can be thickened and filtered to yield magnesium hydroxide. Alternatively, the slurry can be carbonated with carbon dioxide from the calcining kilns to yield a solution of magnesium chloride, which in turn can be reacted with additional slaked, calcined dolomite to precipitate a much purer magnesium hydroxide.

The calcium oxide content of the primary dolomite is credited against the soda-ash branch of the operation. Only this fact makes this an economical process, since 4.6 tons of dolomite is theoretically required to make magnesium hydroxide equivalent to 1.0 ton of magnesia. If the primary magnesium hydroxide is converted to magnesium chloride, which is in turn reacted with calcined dolomite, 4.6 tons of dolomite is still required, but only half of its calcium oxide content can be credited to the soda-ash operation.

By contrast, the other synthetic magnesia processes wherein half or all the magnesia is derived from the magnesium salt solution theoretically require 2.5 tons limestone or 2.3 tons dolomite per ton of magnesia. As a matter of interest, 2.1 tons of pure, natural magnesite and 1.45 tons of pure brucite will each yield 1.0 ton magnesia.

POLITICAL AND COMMERCIAL CONTROL

Since magnesite as a refractory is necessary for the production of steel and nonferrous metals, abundant domestic supplies are a wartime necessity. Dead-burned magnesite was not regularly produced in the United States until World War I. Production of caustic magnesite began in California on a small scale in 1886 but all of that was consumed on the west coast. The year 1910 was the first year in which production (rock mined) reached 10,000 tons. Production of this order continued until World War I shut off supplies of dead-burned magnesite from Austria-Hungary. Production in California nearly trebled in 1915 and by 1917 reached 211,000 tons (crude basis), most of which was dead-burned. The state of Washington, which had not previously been a producer, came into production in late 1916; it produced more than 100,000 tons the next year and subsequently has been the leading factor in the industry. Almost all of the Washington product has been shipped as dead-burned magnesite.

When Austrian magnesite returned to U. S. markets following World War I, the domestic industry could not compete on a price basis and the Washington operations showed no production in 1921. However, under the tariff act of 1922, magnesite was removed from the free list, and the industry has since existed under this protection (Table 1).

Events related to World War II followed a similar pattern but one still differing in vital details. In the decade preceding the war, the United States provided about two thirds of its dead-burned magnesite

and three fourths of its caustic. When the European war shut off exports of magnesite from Central Europe, the needs for dead-burned magnesite were filled for a time by large imports from Manchuria. When these ceased, the domestic industry had already expanded its facilities to the point where no critical wartime shortage developed. It is highly questionable whether foreign producers can ever recapture any appreciable share of the United States market in view of the high quality of the products now produced here.

The self-sufficiency of the United States is based on the natural magnesite deposits of Washington, Nevada, and Texas, and on the synthetic-magnesite plants on the east and west coasts, as well as those based on inland brines.

In 1946, the supplies of synthetic magnesite in the United States accounted for about 65 pct of all caustic magnesite produced and for about 30 pct of all the dead-burned magnesite. Since natural deposits of magnesite are exhaustible, the long-time trend will favor production based on sea water and other brines. However, for dead-burned magnesite it is likely that the deposits of Chewelah, Washington, will be the largest single factor in the industry for many years.

TABLE 1—*Tariff Rates for Magnesite under the United States Tariff Acts of 1922 and 1930, and by Presidential Proclamation*

Act or Proclamation	Tariff, Cents per Pound		
	Crude Magnesite	Dead-burned Magnesite	Caustic Magnesite
Geneva rates effective Jan. 1, 1948.....	$\frac{15}{64}$	$\frac{23}{40}$	$\frac{15}{32}$
Act of 1930, par. 204.....	$\frac{15}{32}$	$\frac{23}{40}$	
Presidential proclamation, effective Dec. 10, 1927.....	$\frac{15}{32}$		$\frac{15}{16}$
Act of 1922, par. 204.....	$\frac{5}{16}$	$\frac{23}{40}$	$\frac{5}{8}$

In the trade agreement with Canada, effective Jan. 1, 1936, provision was made under Paragraph 214 of the Tariff Act of 1930 for the high-lime product of that country as "dead-burned basic refractory material, containing 6 pct or more of lime and consisting chiefly of magnesia and lime." A duty of $27\frac{1}{2}$ pct ad valorem was established on imports of this product. Under the revised agreement with Canada, effective Jan. 1, 1939, the minimum lime content was increased to 15 pct and the duty was lowered to 20 pct ad valorem. The duty on the material containing 6 to 15 pct of lime reverted to the 30 pct ad valorem as provided for in Paragraph 214. A further revision to 15 pct ad valorem became effective Jan. 1, 1948, based on rates established through international agreement at Geneva, Switzerland.

PRICES

Although little crude magnesite is sold, the price range is of interest as reflecting mining costs. There has been little departure in recent years from the price of \$11 to \$14 per short ton that has been reported from West Coast mines. The price of dead-burned magnesite of furnace-maintenance grade, which had fallen to \$22 f.o.b. Chewelah, Washington, in 1930, was increased to \$24 in 1947 and to \$27 in 1948. Dead-burned magnesite sold as periclase grade from West Coast plants was priced at \$35 (90 pct MgO) and \$65 (94 pct MgO), f.o.b. points in the early part of the war, but increases were later granted. When wartime

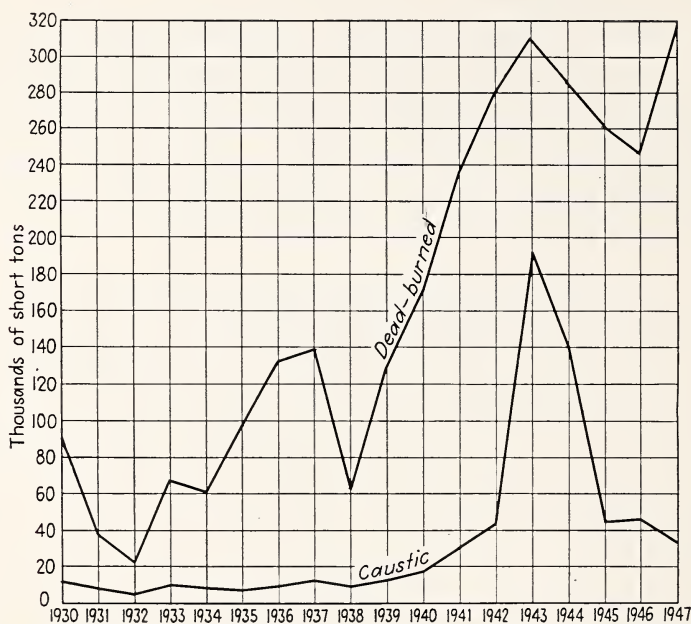


FIG 1—CONSUMPTION OF DEAD-BURNED AND CAUSTIC MAGNESITE IN THE UNITED STATES.
Data from Minerals Yearbook, U. S. Bureau of Mines.

price controls were removed, the price of the 90 pct MgO grade rose to \$40 in 1946 and to \$45.50 in 1947. In most of the 10-year period ending in 1945, caustic magnesite sold for about \$40 per ton f.o.b. West Coast shipping points but by 1947 had risen to \$60 to \$70.

PRODUCTION

The production of magnesite is discussed under various related headings throughout this chapter. The data necessary for a full view of production and use in the United States are shown graphically in Fig 1. Within the period 1930–1947, the dead-burned magnesite industry

closely reflected the trends of heavy industry, particularly steel. The consumption of 311,000 tons in 1943 included only 9000 tons of imported magnesite. During that year, the U. S. production from natural magnesite rock was 186,000 tons. A fact revealed by Government data is that while only 4.1 lb of dead-burned magnesite was consumed per ton of steel production in 1930, the figure had risen to 6.5 lb in 1945. Thus magnesite has improved its relative position. Domestic production of dead-burned magnesite reached an all-time peak of 315,000 tons in 1947.

Caustic magnesite, the consumption of which was approximately 10,000 tons annually before World War II, has greatly increased its market, owing to new uses. The very high level of production and consumption during the war was largely accounted for by the operations near Gabbs, Nevada, from which the plant producing metallic magnesium at Las Vegas was supplied.

TESTS AND SPECIFICATIONS

Crude Magnesite—Crude magnesite has been used in small tonnages for preparation of certain chemicals such as epsom salts but the total annual use of crude magnesite in the United States is less than 2000 tons.

Caustic Magnesite—Magnesite for oxychloride cement is tested for the purpose by making test slabs of the cement. The magnesites are purchased from suppliers on the basis of character of the test specimens in addition to specifications covering chemical and physical analysis. The general specification for caustic magnesia used in cements is as follows: MgO , 90 pct min.; free CaO , 2.5 pct max.; R_2O_3 plus SiO_2 , not particular but should be low; ignition loss, 3 to 4 pct; color, uniform; grain size, 90 pct minus 200-mesh.

Chemically combined limes such as silicates are not harmful but free CaO causes the cements to expand and crack during setting.

In 1947, the American Society for Testing Materials organized a new technical committee known as Committee C-2 on Magnesium Oxychloride Cements and the American Standards Association formed a Sectional Committee A-88 on Magnesium Oxychloride Cement Flooring.³ The scope of these two committees will cover specifications, testing, definitions, application and research pertaining to such cements.

Magnesite for fertilizer is sold on the basis of MgO content; therefore most magnesia sold for this purpose has more than 90 pct MgO and much of it has more than 95 pct MgO . It should be ground but granular, should contain a minimum of free CaO , and should have an ignition loss of between 3 and 5 pct. Even though the magnesia may appear satisfactory from a chemical and physical point of view, it is extensively tested in small lots before large-scale application is made.

Specifications for caustic magnesia for use in the production of synthetic rubber are varied, depending on the use and on arrangements between buyer and seller. Typical specifications are given in Table 2.

TABLE 2—*Typical Specifications for Caustic Magnesia*

Specification	Heavy Caustic	Extra Light Caustic
Size.....	All through 100 mesh	All through 100 mesh
Color.....	Buyer's standards	Buyer's standards
MgO, pct.....	87.0 min.	92.5 min.
CaO, pct.....	2.5 max.	2.0 max.
SiO ₂ + R ₂ O ₃ , pct.....	4.0 max.	1.1 max.
Ignition loss, pct.....		4.5 max.

The specifications for other uses of caustic magnesia are as varied as the uses. In general, high degrees of purity are required with particular emphasis placed on low CaO content. These magnesias are ground to prescribed sizes. Like most caustic magnesia, these magnesias are sold in 100-lb bags.

Dead-burned Magnesite—Dead-burned magnesite is also subjected to both physical and chemical tests. The nature of the requirements is somewhat dependent upon the uses to which the material is put. If it is to be used as grain magnesite for building up monolithic bottoms in the basic open-hearth furnace, certain characteristics are desired that would be unnecessary in dead-burned magnesite from which brick are to be manufactured. Both services require a dense, well-burned grain with a predominance of large sizes.

Grains intended for the open-hearth bottom preferably contain a reasonable amount of silica (in the form of silicates), which aids the process of sintering the hearth to form a monolithic flooring. However, excessive amounts of lime and other impurities are undesirable, since magnesium oxide is the constituent that offers greatest resistance to solution by open-hearth slag. Lime, when present in large percentages, may combine with silica to form dicalcium silicate ($2\text{CaO} \cdot \text{SiO}_2$), which under certain conditions undergoes a rapid inversion that may reduce the magnesite to dust. Its complete stabilization is possible, however, and has been accomplished in products that contain it.

Iron oxide, which is preferably kept low in caustic magnesite, is not an undesirable constituent in dead-burned magnesite. It aids the process of dead burning, gives a grain of greater density, and probably gives the individual grains greater powers of coherence. The major tonnage of dead-burned magnesite, used for maintenance of furnace hearths, contains 4 to 5 pct Fe_2O_3 . In the magnesite from Austria and Czechoslovakia, this is a natural impurity present in the breunneritic type of crystalline magnesite. In the United States and Canada, the iron

oxide is added as kiln charge in the form of finely powdered roll scale or iron ore.

Synthetic magnesites contain the same impurities as natural ones but the manufacturers have chosen to follow certain departures. Iron oxide may be added but frequently is omitted. Synthetic magnesites that contain less than 2 pct CaO frequently contain added SiO_2 to give a total of 5 pct, which, after burning, would in part be present as forsterite ($2\text{MgO} \cdot \text{SiO}_2$). This is particularly typical of the California products. The term periclase, which refers to the crystalline mineral MgO , and which predominates in all dead-burned magnesites, has come to denote generally in the trade a dead-burned, low-iron magnesite showing more than 90 pct MgO by analysis.

MARKETING, USES AND PRICES

Caustic Magnesite

As the graph of total consumption shows, the use of caustic magnesite has increased steadily since 1938. For 1946, a new peak for uses other than in the manufacture of metallic magnesium was reached over the previous high in 1924. The production for the years 1942, 1943, and 1944 includes about 6400 tons, 135,800, and 104,000 tons, respectively, of caustic magnesite used for making metallic magnesium. Aside from this wartime consumption, other factors have tended to stimulate the production of caustic magnesite. One factor is the increase in the use of magnesium oxychloride cements for interior flooring. The addition of copper powder to the cement has vastly increased resistance to weathering and cracking.¹²

The cement is used mainly for flooring. Such flooring is resilient, fireproof, spark-proof, and vermin-proof. It can be installed over wood, and it can be sawed and nailed without damage. Minor amounts of oxychloride cements are used in small decorative moldings, wallboard, caskets, and as an abrasive binder. The cements are prepared on the job by mixing a solution containing about 20 pct MgCl_2 with dry, ground, caustic calcined magnesite. Variable amounts of fillers such as wood fiber are added.

In 1944, the Dow Chemical Co., Westvaco Chemical Division, and F. E. Schundler and Co. formed the Oxychloride Cement Association in Washington, D. C. This organization supplies materials and information relating to such cements.

Another factor leading to increased production of caustic magnesite is the heavily increased demand for magnesium compounds in fertilizers.²² Magnesia and magnesium compounds serve two purposes in fertilizers; one is to supply Mg as such to the plant; the other is to assist in the assimilation of phosphorus. The magnesia is rarely added

alone but is added as a constituent of a balanced, formulated fertilizer.

Other major uses of caustic magnesia are in the manufacture of synthetic rubber, in which operation it is used for both catalyst and filler, and in the manufacture of magnesium chemicals. Miscellaneous uses are as coatings for welding rods, fillers for heating elements, reagent for reduction of silica in boilers, pharmaceutical purposes, glue compounds, glass constituent, and fine abrasives.

Accurate consumption figures for these various uses are difficult to obtain, but in 1942 about 48 pct of U. S. consumption was in oxychloride cements, 10 pct in synthetic rubber, 11 pct in fertilizers and 31 pct in miscellaneous uses. Current figures are probably about 30 pct for cements, 25 pct for fertilizers, 10 pct for rubber and 35 pct for miscellaneous uses.

The price of caustic magnesite depends on MgO content and preparation for the trade. Ground and bagged magnesite generally costs about \$6 more per ton than unground, bulk magnesite. The average price per ton for all grades of caustic magnesia, except those in the chemical grades, has increased steadily from \$34.81 in 1941 to \$63.81 in 1946.

Dead-burned Magnesite

Dead-burned magnesite is used almost entirely for the manufacture of refractories, sold as grain products or as shaped brick. These refractories are used throughout industry but find their largest markets in the steel and copper industries. The hearth of the basic open-hearth steel furnace may be built up by burning in layers of magnesite grains or by using a monolithic, cold-setting, ramming mix of magnesite grains to which a bonding agent has been added.

Brick resistant to basic slags may be made of magnesite alone or of mixtures of magnesite with chrome ore or olivine. Such refractories have been greatly improved in quality, so that their use is no longer confined to hearths and side walls but has been extended to roofs of such high-temperature furnaces as the copper smelter and the open-hearth steel furnace.

OTHER MAGNESIUM COMPOUNDS

Beside the magnesium oxides discussed under refractory and caustic headings, an impressive variety of other magnesium compounds is currently being produced. The use of these compounds is increasing and continued substantial production is anticipated as new outlets are developed.

Magnesium sulphate has been made by leaching serpentine and olivine with sulphuric acid, by extracting it from certain well waters, and mainly by reacting caustic magnesite with sulphuric acid. This

last method accounts for the bulk of the production. Purity of product is governed by purity of raw materials and by processing techniques. Low-grade sulphate is used for fertilizer and stock feed. High-grade sulphate is used for coagulating rayon in the Viscose process, for weighting and dyeing textiles. Special grades find use as a medicine and chemical reagent.

The production of magnesium sulphate of all grades on a 100 pct MgSO_4 basis has been in excess of 25,000 tons per year during the period 1942 to 1947. The average value has been about \$50 per ton.

Magnesium chloride has been obtained from well brines, from natural salts such as carnallite, by conversion of magnesium hydroxide from sea water, and by reaction of caustic magnesite with carbon and chlorine. The largest consumption of this salt is in the manufacture of metallic magnesium and oxychloride cements. After curtailment of the wartime magnesium-metal program, the production of magnesium chloride decreased from a 1943 peak of 640,708 tons to 32,137 tons in 1946. Production seemingly is stabilized at about this figure. Price has increased somewhat; in 1945, it was \$32 per ton of flaked magnesium chloride; in 1946, it was \$37.

Magnesium carbonate is prepared by precipitation from solutions of magnesium bicarbonate. Most of the technical grade is obtained from dolomite by use of the Pattison process, although a substantial tonnage is being produced on the West Coast by the carbonation of magnesium hydroxide. Much of this production is used in the manufacture of insulation of all types. Special grades of pure carbonate are used as rubber compounders, as ink, paint, pigment and varnish ingredients, and as an additive to prevent moisture adsorption by hygroscopic substances.

The production of precipitated magnesium carbonate has decreased from 55,207 tons in 1943 to 47,423 tons in 1946. The price has fluctuated between 6¢ and 8¢ per pound.

Magnesium silicate, as part of the natural mineral olivine, is being exploited commercially for refractory purposes. Olivine is composed of forsterite, $2 \text{MgO} \cdot \text{SiO}_2$, and fayalite, $2 \text{FeO} \cdot \text{SiO}_2$; fayalite is the minor ingredient and generally averages about 15 pct of the olivine. Olivine is quarried on a relatively small scale. Hand cobbing and sorting may be used to remove deleterious talc and serpentine impurities. For refractory purposes, these low-melting minerals are reacted with magnesia.

Olivine is a common constituent of igneous rocks, but deposits of sufficient purity to be commercial are not plentiful. Deposits in North Carolina have been worked continuously since about 1935. These deposits are contaminated in varying degrees and the ore requires close sorting for use in refractories. The state of Washington has a deposit near Bellingham that can be literally described as a "mountain of ore."

The olivine is massive and relatively unaltered. Unfortunately, the geographic location has prevented anything but small, preliminary development.

Olivine and serpentine have been utilized as a fertilizer ingredient and as raw material for the preparation of magnesium sulphate and chloride. Many thousands of tons of serpentine have been used in New Zealand in recent years to increase the availability of phosphorus in phosphate fertilizer.

Synthetic magnesium silicate with high absorptive properties is being manufactured by Westvaco Chemical Division at its Charleston, West Virginia, plant (private communication). Substantial tonnages of this product are being made by reaction between precipitated calcium silicates and magnesium chloride solution.

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CHAPTER 25

MANGANESE ORE

BY GORDON H. CHAMBERS*

MANGANESE ore is a true jack-of-all trades among industrial minerals, its only possible rival being iron ore. It is used in porcelain enamel, dry batteries, building brick, glazed pottery, floor tile, plastics, welding rods, chemicals, and varnish. You may be reading this through spectacles decolorized with manganese, and the light bulb above you contains some of this element.

GEOLOGY

Nearly all commercial manganese oxide deposits are of secondary origin; that is, they are concentrated by weathering from other manganese minerals more sparsely distributed in veins. The oxide minerals usually form irregular masses but in some places (Russia) they occur as beds of varying thickness and purity. Some manganese oxide bodies occur in soft gravel or clay formations but in other places the minerals are found in the form of veins and rounded nodules in limestone and other hard rocks. The geologic features of manganese deposits closely resemble those of iron deposits. Classification of the deposits is shown in the following table:

- I. Classification of manganese deposits based upon form of occurrence
 - A. Stratiform masses
 1. Oxides interlayered with sediments or layered volcanic or metamorphic rocks
 2. Carbonates or silicates interlayered with sediments or layered volcanic or metamorphic rocks
 3. Oxides, as surface bog deposits
 - B. Veins and breccia filling
 1. Oxides in larger part
 2. Carbonates or silicates partly weathered to oxides
 - C. Irregular masses
 1. Oxides
 2. Carbonates or silicates largely weathered to oxides
 - D. Aggregates of small oxides in clay or weathered rocks
 1. Mainly oxides
 - E. Unclassified deposits
- II. Classification of manganese deposits based upon mode of origin
 - A. Hydrothermal deposits

* Vice President, Foote Mineral Co., Philadelphia, Pennsylvania.

- B. Sedimentary deposits
C. Residual concentrations
D. Metamorphosed deposits

COMPOSITION AND PROPERTIES

Composition—Typical analyses of manganese ore are given in Table 1.

TABLE 1—*Typical Analyses of Manganese Ore*

Constituents	Composition, Pct ^a					
	Caucasian	Gold Coast	Indian	Mexican	Moroccan	Phillipsburg, Montana
MnO ₂	86.00	85.14	85.94	85.46	86.15	70.00
MnO.....		3.31			0.90	
SiO ₂	5.00	2.01	1.32	1.94	3.30	12.0
Al ₂ O ₃	1.75	2.32			0.68	1.25
TiO ₂		0.06				
CaO.....		0.07		1.02	1.68	
BaO.....		0.11			0.70	
K ₂ O.....		0.57				
V ₂ O ₅		0.06				
P.....		0.07		0.014		
CO ₂		0.06			2.52	
H ₂ O.....		2.95				
Cu.....	0.03	0.02		0.05	0.18	
As.....	0.01	0.06				
Sb.....		0.02				
Pb.....	tr	tr	0.02	0.94	0.51	
Fe.....	0.75	1.40	2.47	0.45	0.69	2.25
Ni.....	0.05	0.03				
Co.....	0.01	0.028				
S.....				0.03		
Zn.....				0.03		
MgO.....				0.34	1.08	

^a Java, the Philippines, China, and Japan have not resumed production or export.

Properties—The mineralogy of manganese is extremely complex and more than 100 manganese minerals have been listed. The identification of the manganese oxide minerals has been ably defined by Fleischer and Richmond.⁵ Practically all of the manganese oxide of commerce is composed largely of two minerals, psilomelane and pyrolusite, which commonly are intimately mixed in the same ore deposit. Commercial ore ranges from minerals that are sooty and soft enough to soil the fingers when handled to hard crystals that are brownish black or gun metal in color. Its chemical composition ranges from manganese dioxide to mixtures of manganese dioxide with lower oxides of manganese,

and the minerals always include impurities such as silica, iron, lime, barium oxide, and combined water.

DISTRIBUTION OF DEPOSITS

Manganese ore is widely scattered in all parts of the world in many types of deposits but relatively few can be mined profitably. The three most important producers at the present time are Russia, African Gold Coast, and British India. These major sources have immense reserves and could normally supply the entire amount consumed in the world. Other important factors in the world market are Brazil, South Africa and Mexico.

PRODUCTION AND IMPORTS

The world production of manganese averaged 5,334,000 tons yearly for the 3-year period of 1938, 1939, and 1940. During the same 3 years, the United States produced only 9.7 pct of the world output of standard manganese ore, in spite of the large market here and a protective tariff. Manganese is one of the few essential raw materials for which we must depend primarily upon foreign sources of supply. In normal business years, the United States probably will require 1,000,000 short tons of manganese ore annually. This estimated postwar consumption is about 50 pct larger than the average requirements for manganese ore during the years 1935-1939. Recent production of manganese ore in the United States is reflected in Table 2.

TABLE 2—*Manganese Ore Produced and Shipped from Mines in the United States, 1943-1947^a*
SHORT TONS

Manganese Ore	1943	1944	1945	1946	1947
Mine shipments of battery ore.....	9,973	6,224	8,042 ^b	8,295	6,189
Mine shipments of metallurgical ore.....	195,096	241,170	174,295	134,381	125,428
Total mine shipments, 35 pct or more Mn.	205,173	207,616	182,337	143,635	131,627

^a U. S. Bureau of Mines Mineral Market Report No. 1633, July 29, 1948.

^b Includes small quantity of miscellaneous ore.

Imports of all grades of manganese ore (35 pct or more Mn) into the United States during 1947 for consumption amounted to 1,297,992 short tons, containing 624,431 tons of manganese and having a value of \$21,291,181. These imports included 67,563 tons of battery and chemical grade ore from the seven countries listed in Table 3.

PREPARATION FOR MARKET

The lump ore intended for chemical or ceramic use is generally hand-sorted either at the mines or at the grinding plant. Pieces of limestone, clay and limonite are carefully removed either by hand or by one of the customary concentration methods. Each lot of ore is analyzed

TABLE 3—Imports of Battery and Chemical Grade Ore for Consumption in the United States during 1947^a

FROM	SHORT TONS
Gold Coast	49,169
USSR	15,808
India	1,075
Chile	574
Peru	448
Portuguese Guiana and Angolo	448
Mexico	41
Total	67,563

^a U. S. Bureau of Mines Mineral Market Report No. 1633, July 29, 1948.

before it is processed. The manganese ore first passes through an oil-fired rotary drier, then the lumps are reduced to $\frac{3}{4}$ -in. size in a jaw crusher. Some trades—for instance, battery and brick manufacturers—require a granular product, and for these consumers the manganese is further crushed in roll-type grinding units and then screened to exact specifications. Other users prefer a finely powdered, air-floated material. This is produced in ball-race mills connected in closed circuit with an air classifier. The final product is so fine that 80 or 90 pct passes a 325-mesh screen.

COMMERCIAL USES

The principal use for manganese ore, of course, is in the steel industry, but as this book is restricted to nonmetallic minerals, only its nonmetallurgical uses will be discussed.

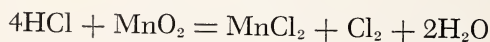
Dry Batteries—The battery industry in the United States uses thousands of tons of manganese annually as a depolarizer in dry cells. The author roughly estimates that the battery industry in the United States consumed 30,000 tons of high-grade manganese ore in 1945. The ores for use in batteries may be tested under the methods prescribed by the National Bureau of Standards. One theory is that the best results are obtained from manganese with a high percentage of combined water and low lime content. It is also believed that ores containing very little copper, nickel and other heavy metals are best for battery use. Recent studies indicate that the crystal structure of the manganese ore is also a factor. In recent years, synthetic manganese dioxide, produced by either electrolysis or normal precipitation of manganese salts, has been used as a partial substitute to improve the "shelf life" of the battery.

Manganese Sulphate—Several manufacturers produce this manganese sulphate in the United States and almost every one of them has developed a different method of production. In one of the older methods, finely powdered ore is mixed with concentrated sulphuric acid to form a stiff paste. This is heated in a furnace and the soluble

manganese sulphate is leached out and evaporated. This salt serves as a starting point in the manufacture of fertilizer and manganese driers.

Fertilizers—There has been a steadily growing use for manganese sulphate as a fertilizer in limestone and muck soils. Prior to 1930, the Florida Agricultural Experiment Station conducted some extremely interesting experiments with this salt. They found that truck crops such as tomatoes, beans, potatoes, and corn failed to fully mature in the high-lime glade soils when treated only with commercial fertilizers, but the same soils produced healthy, profitable crops when a definite percentage of manganese sulphate was added;²³ for example, 50 lb of manganese sulphate per acre increased the yield of snap beans 400 pct and the quality of the beans was much better. With Irish potatoes, the yield was two to three times as great as that secured without manganese. Originally the use of manganese sulphate in agriculture was confined largely to southwest Texas and Florida but now it is being used in other states as a minor mineral in fertilizers. Dr. A. F. Camp, of the University System of Florida, says that "without additions of manganese or the presence of available manganese, which is very limited in the natural state in Florida, no proper growth of citrus can be maintained in that state. This manganese deficiency is specific and no other chemical element can replace its action in the proper nutrition of the orange, grapefruit, or tangerine plants." For the near future, the industry expects to sell about 30,000 tons of manganese sulphate annually, a fourfold increase in the last few years.

Manganese Chloride—Manganese chloride is a rose-red, hygroscopic, crystalline salt. It is soluble in water and picks up moisture from the atmosphere so readily that it must be kept well covered. Manganese chloride is produced in the United States on a moderate scale, but the process here involves reducing the ore to MnO and then treating this material with hydrochloric acid. It is a by-product of some of the old chlorine plants in Europe. Manganese dioxide is such a strong oxidizing agent that it will decompose hydrochloric acid and evolve chlorine. This property is the basis on which these old European chlorine plants operate. The simplified reaction is as follows:



The by-product manganese chloride is used in producing black flashed brick and in making some manganese driers.

Manganese Driers—Manganese dioxide and certain manganese salts are used as driers in varnish, japan, and printing ink. Linseed oil and other oils used in varnish dry by oxidation and the rate of oxygen absorption of the oils is increased by the addition of manganese. It is such a powerful drier that 0.25 pct is usually the maximum amount

added to linseed oil. The manganese can be introduced in the varnish as the linoleate, the resinate, the borate, the naphthenate, the sulphate, or the precipitated dioxide. In many of the old types of japan and varnish, finely powdered manganese oxide is used.

Hydroquinone—Manganese dioxide is employed as an oxidizing agent in the manufacture of hydroquinone. For this use, the ore must be very finely ground and must have a physical structure that permits rapid reactions and good solubility in sulphuric acid. Hydroquinone is principally used as a photographic developer for both still and moving-picture film. It has minor uses as a powerful medicinal antiseptic.

Potassium Permanganate—The purple crystalline salt, potassium permanganate, is another of the products made from manganese ore. It is soluble in water, producing a solution with intense reddish violet color. It is a strong oxidizing agent for organic and inorganic substances and its chemical uses cover a wide range from dry-cleaning shops to lithopone and electrolytic-zinc plants. Moderately large quantities are sold for use as a disinfectant.

Glass—Manganese imparts a lavender tint to glass, which neutralizes the yellowish green color due to traces of iron in the sand and other batch materials. In some cases, 1 lb of manganese dioxide is sufficient to decolorize a 2500-lb batch. However, glass decolorized with manganese has the curious property of sometimes changing to pink on long exposure to light. For this reason, during the past 30 years, it has been largely replaced by selenium in glass decolorizing. In optical and lamp glass, it is still frequently used. If excess manganese is added, the glass becomes deep purple or black. Some theorists say that it is impossible to produce a true black glass or black glaze but a mixture of manganese and either iron or chrome oxide is so nearly perfect that all but the theorists are satisfied. The black glass used in stemware, in ornamental objects, and in bottles derives its color from manganese. Manganese also colors the flat or plate glass used in black table tops, store fronts, and wall panels.

Porcelain Enamel—Some shades of dry-process enamel bathtubs contain small quantities of manganese dioxide and it is employed to a larger extent in the wet-process enamel applied on teakettles, refrigerators and enameled signs. It is particularly useful in ground-coat enamels, as a combination of cobalt and manganese has the peculiar and valuable property of bonding with the steel base. A typical ground coat may contain 0.5 pct cobalt and 1.5 pct manganese.

Gray Brick—Manganese is used to produce the beautiful gray speckled brick for public buildings, hotels, schools, and homes. For this purpose a metallurgical type of manganese ore is satisfactory, but it must be granulated and screened to exact specifications. Slight variations in screen size show up plainly after the brick are burned, be-

cause the particles of manganese fuse to several times their original size. Brick manufacturers usually add from 25 to 60 lb of manganese per thousand brick. It is employed primarily to neutralize the yellowish buff color of the clay. The secondary purpose is to provide specks, which give the brick a lively appearance. Manganese was first used in brick some 50 years ago by a small plant at Union Furnace, Ohio. Since that time there has been no marked change in the process.

Black Brick—The best black brick are produced by the use of manganese. Sometimes the entire clay body is colored by the addition of 80 to 120 lb of finely powdered manganese oxide per thousand brick. This method is rather expensive and therefore the majority of the manufacturers flash their brick. A good, blue-black flash can be put on the surface of the brick by throwing manganese in the fireboxes at the end of the burn. The kiln is first given a heavy smoke flash for several hours. The manganese dioxide is mixed with common salt and 8 to 10 lb is spread on each fire. A half hour later a second shovelful is added to the fires, and sometimes a third round is used. During the flashing period, the kiln should be in a moderately reducing condition and the temperature should be at least 1850°F. After the flash, the kiln is cooled rather rapidly. The best results are obtained with air-floated manganese ore, as this is more thoroughly circulated in the kiln than a coarser product and consequently produces a larger percentage of flashed brick. Manganese chloride is used also to produce a fine jet black flash. It volatilizes easily on a hot fire and often can be used successfully on brick that will not withstand the higher temperatures necessary with manganese dioxide.

Pottery and Tile—The coloring value and stability of manganese oxide at all firing temperatures were discovered and appreciated many years ago by the pottery trade. It imparts a strong brown color to ceramic glazes; for example, the chocolate-brown glaze on porcelain insulators for high-tension lines is often produced by a mixture of manganese, chrome, and red iron oxides. It is also the principal colorant in brown earthenware jugs and garden pottery. Manganese oxide is such a reliable raw material that it is hard to find a ceramic manufacturer who does not employ it to some extent either in the glaze or in the body. For the latter, its application is similar to its use in gray and black brick. Plants that manufacture terra cotta and floor tile mix carefully granulated manganese oxide with the clay to produce a gray, speckled effect. When black floor tile are desired, it is possible to get a fairly good shade with red clay by the addition of 2 to 4 pct finely ground manganese ore. Using buff clay, a good brown can be obtained with 2 pct manganese chloride.

Welding Rod—Manufacturers of coated welding rod use a wide variety of materials in the coating composition. Two of the common in-

gredients in a coating formula are manganese carbonate and manganese dioxide. Their principal purpose is to produce a brittle, fluid slag, and to replace the manganese that is volatilized in the arc.

Minor Uses—From a chemical standpoint, manganese is remarkable in that it shows valences of 2, 3, 4, 6, and 7 in different compounds. It forms a wide variety of salts, some of which have small commercial uses. For example, barium manganate is a green pigment, manganese arsenate is an insecticide, and manganese phosphate is a protective coating for steel.

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CHAPTER 26

MICA

BY EUGENE H. DAWSON*

MICA is a mineral that once was a familiar sight as fireproof windows in stove and furnace doors and as lamp chimneys and shades. Since 1878, the beginning of the electrical age, the use of mica for such purposes has gradually declined and its use in electrical equipment and appliances has developed to such an extent that the known sources of supply are scarcely equal to the demand.

With the increasing capacity of electric generating units, the size of mica sheets found in nature was inadequate. However, in 1894, a process was developed whereby thin films or splittings cemented with shellac or other binders could be pressed into large sheets.¹⁸

The introduction of radio in the early 1920s created such a heavy demand for the smaller sizes of mica that on March 22, 1938, mica was included among 23 commodities on the list of strategic materials approved by the United States Army and Navy Munitions Board. To be included in this list, the material must be one whereof the domestic supply is not sufficient to meet the demand.

COMPOSITION

Mica is a complex mineral composed principally of the silicates of potassium, aluminum, and magnesium. Less prevalent species contain, as essential components, lithium, vanadium, and chromium. Iron usually is present either as an essential component or as an impurity.

The mica group comprises some nine different species, five of which, muscovite, phlogopite, vermiculite, lepidolite, and biotite, are widely used in industry. Lepidolite and zinnwaldite (lithium micas) and roscoelite (vanadium mica) are sources of lithium and vanadium.

Muscovite, "white mica," is potassium mica. Theoretical formula⁶ $\text{H}_2\text{KAl}_3(\text{SiO}_4)_3$. There are two varieties, distinguished as to color, known in industry as ruby and green. In crystals or "books," the colors each range through varying shades of red and green. However, when split into thin films, all micas, except biotite and phlogopite, are colorless and transparent. Muscovite frequently is stained red or black by thin films of iron oxide between the laminae. The staining usually is derived from magnetite, which sometimes is found as unaltered crystals.

* Consulting Mining Engineer, New York, N. Y.

Phlogopite is magnesium mica. Theoretical formula is $(\text{H,K,Mg,F})_3\text{-MgAl}(\text{SiO}_4)_3$. In the trade, this variety is known as "amber mica," from its color, which ranges from pale yellow to dark brown, with a pearly luster.

Vermiculite's theoretical formula is $(\text{OH})_2(\text{Mg,Fe})_3(\text{Si,Al,Fe})_4\text{-O}_{10}\cdot 4\text{H}_2\text{O}$. It may be regarded as a hydrated biotite. Usually it occurs as aggregates of wavy bronze-yellow flakes.

Biotite, "black mica," is magnesium iron mica. Its theoretical formula is $(\text{H,K})_2(\text{Mg,Fe})_2\text{Al}_2(\text{SiO}_4)_3$. The iron content is variable and with decreasing amounts of iron it grades into phlogopite. The color is from dark brown to black.

Lepidolite is lithium mica. Theoretical formula is $\text{KLi}(\text{Al}(\text{OH,F})_2)\text{-Al}(\text{SiO}_3)_3$. It has a variable ratio of fluorine and hydroxyl. It usually occurs as aggregates of fine flakes in colors from pale lilac to deep purple.

Zinnwaldite, lithium-iron mica, with theoretical formula of $(\text{K,Li})_3\text{FeAl}_3\text{Si}_5\text{O}_{16}(\text{OH,F})_2$, is one of the rarer micas. It seldom occurs except in small flakes in colors from gray to smoky brown. Its only use is as a source of lithia.

Roscoelite, vanadium mica, has a theoretical formula of $\text{H}_3\text{K}(\text{Mg,Fe})(\text{Al,V})_4(\text{SiO}_3)_{12}$. It is a rare mica, found as fine flakes colored in various shades of green and brown.

PROPERTIES

All micas crystallize in the monoclinic system, usually in the form of flat, six-sided crystals with the elongation in the direction of the vertical axis. The basal cleavages of muscovite and phlogopite are nearly perfect, permitting the crystals to be split into thin sheets or films 0.0001 in. thick or less. These films have such strength and flexibility that in the higher qualities they may be wrapped around a mandril $\frac{1}{8}$ in. in diameter without rupture. The cleavages of biotite and lepidolite are usually poor; they may not be even, nor continue across the entire crystal.

Micas vary in hardness ranging from 2 to 2.5 for the softer phlogopites and from 3 to 3.5 for high-iron varieties. All micas yield water when strongly heated, usually about 5 pct, which probably represents the water of crystallization. An exception to this is vermiculite, which contains from 11 to 21 pct water and is definitely hydrated. Vermiculite when heated expands in one direction only; that is, at right angles to the cleavage. The volume many increase up to 16 times the original.

For all ordinary uses, mica is unaffected by acids and is infusible. Muscovite can be used for electrical purposes where the temperatures are not in excess of 1000°F. Phlogopite will withstand temperatures up to 1850°F.

Muscovite and phlogopite micas have high dielectric strengths; i.e.,

the property of withstanding high voltages without puncture. This is measured in volts per mil of thickness at 70°F. The results of extensive breakdown tests on micas from various parts of the world show for muscovite from 3.3 to 8.5 kv and for phlogopite from 4.3 to 5.9 kv.⁹

The power factor of mica is the ratio of the total power loss in a capacitor in which it is the dielectric to the total volt-amperes supplied to the capacitor. The power factor of a mica determines its suitability for use in capacitors, since a mica with a high power factor generates much heat whereas one with a low power factor but little heat. The power factors for clear muscovites from India and the United States range from 0.01 to 0.02, for slightly stained muscovite, from 0.01 to 0.21 for heavy stained muscovite, 0.82 to 5.4, and for phlogopite, from 0.38 to 7.12.

The dielectric constant of mica is the ratio of the capacitance of a capacitor in which it is the dielectric to the capacitance of a similar capacitor in which the dielectric is a vacuum.

ORIGIN AND MODE OF OCCURRENCE

Mica has a wide distribution throughout the world. Muscovite and biotite are essential constituents of granites, schists, and similar rocks. In crystalline igneous rocks, mica is present as a primary mineral but in metamorphic rocks it is usually secondary. The total quantity of mica in schists, gneisses, granites and other rocks is enormous but, occurring as it does in small crystals or flakes, it has no value in industry except in rocks that contain 5 pct or more, which sometimes are used as a source of scrap mica.

Muscovite, the principal mica of industry, is found in acid pegmatites, of which two characteristics are coarseness of texture and a notable uneven segregation of their constituent minerals. Muscovite usually occurs as tabular crystals, hexagonal in outline, with prismatic faces more or less striated horizontally. These crystals may be up to 8 ft in diameter or less than $\frac{1}{16}$ in. across. A notable example of large mica crystals was discovered at the Purdy mine¹⁴ near Mattawa, Ontario, in 1941. One crystal measured 7 by 9.5 ft and was nearly 3 ft thick. This book yielded about 7 tons of trimmed sheet. Mica crystals like those found at the Purdy deposit are unusual; sheets 12 to 18 in. across represent the largest sizes normally found.

Lepidolite or lithia mica is confined to granite pegmatites whose source magma was rich in lithia. Such pegmatites are distinctly regional in their distribution.

Biotite is abundant in schists and sometimes found in granite pegmatites, occasionally associated with muscovite; more rarely, intergrown with the latter. Muscovite is generally rare or absent in biotite-rich dikes.

Vermiculite, considered an altered biotite, has the same origin.

However, at Libby, Montana,¹³ vermiculite occurs as a stock of irregular mica crystals ranging from 1 to 6 in. across. The deposit is cut by numerous narrow dikes of igneous rock, which apparently altered a rich concentration of biotite.

Phlogopite is restricted to basic pegmatites and crystalline limestones composed principally of the mineral pyroxene, and is essentially quartz free. There are but few areas in which commercial deposits of sheet phlogopite are known.

SOURCES

The important producing countries of muscovite mica, listed in the order of their importance, are: India, Brazil, United States, and Argentina. Smaller quantities have been produced intermittently in Canada, Madagascar, Peru, Bolivia, Australia, Rumania, Norway, Spain, and Portugal. No data are available for Soviet Russia but apparently it has sufficient mica production to meet its own needs.

The two countries with the longest records of production are India and the United States. Production commenced in New Hampshire in 1803 at a mine that again produced mica in 1943. Mica has been produced from 23 states of the Union, the five principal producers being North Carolina, New Hampshire, South Dakota, Georgia, and Connecticut. Other producing states, which in 1944 provided but 9.5 pct of the total of uncut mica larger than punch, are Alabama, Arizona, Colorado, Idaho, Maine, Massachusetts, Montana, New Mexico, Pennsylvania, Virginia, and Wyoming.

India has been the principal source of the world's supply since 1885. The occurrence there of numerous deposits bearing commercial quantities of mica and an abundance of low-cost labor has permitted India to maintain dominance in the markets of the world. In 1929, India furnished 75 pct of the reported production of block mica in the world; in 1935, it furnished 83 pct.

The deposits in India are not richer in the proportion of mica recovered to the rock mined nor in the proportion of the better qualities of mica produced in the United States and other countries, but the deposits have been mined to greater depths because of the low cost of labor. India is almost the only source of muscovite splittings, although in recent years small quantities have been produced in Mexico, the United States, and Brazil.

Brazil has become second only to India in the production of block mica. However, the quality of finished sheet is below that of India, as Brazilian labor has not as yet acquired the skill of experienced Indian operators. Argentina has furnished substantial quantities for a number of years but a large percentage has been of low quality not suitable for first-class electrical uses.

Scrap mica is obtained as a by-product from the preparation of

crude blocks for sheeting, the trimmings and scalings in sheeting, the leavings after punching, the waste from splittings, and from mining weathered pegmatite dikes, which contain commercial quantities of mica in the form of small crystals. Some dikes in Franklin district, North Carolina, are reported to contain as much as 10 pct mica. It is produced also from rich biotite-mica schists. North Carolina is the principal source of scrap from mining weathered pegmatites, where it is recovered also by washing the residues from kaolin mining operations.

Vermiculite is a comparatively rare species of mica, of which the largest known deposit is at Libby, Montana. Other deposits are reported in Colorado, Wyoming, North Carolina, South Carolina, and Georgia.

Lepidolite has been mined in California and South Dakota for its lithium content. Other deposits are reported in New Mexico.

Roscoelite, the rare vanadium mica, occurs in sandstones near Rifle and Placerville, Colorado; also in adjacent areas of Arizona and Utah. These deposits have been mined to a considerable extent for their vanadium content. In Alabama, roscoelite occurs in graphitic schists and the deposit is reported to be of considerable magnitude.

USES

Muscovite mica of first quality is vitally essential as the dielectric in capacitors for radio and radar circuits, as the dielectric in magneto-capacitors and coils, and as insulation in aircraft spark plugs. Practically every radio tube contains one or more pieces of mica, used as an insulation spacer for filaments, as plates, and as supports for wires in making the tube assembly. Other uses that require relatively small quantities, but which are of the utmost technical importance, are insulation for high-voltage lamps, gauge-glass gaskets for high-pressure boilers, in special metal-casting processes, view plates in metallurgical furnaces and diaphragms for oxygen breathing equipment.

Muscovite mica of lower grades, sometimes called "electric mica," is used extensively in the manufacture of toasters, waffle irons, hot plates, coffee pots, and many similar products for household use.

Muscovite and phlogopite mica splittings are used for making built-up mica insulation products such as mica cloth and tape and mica plate. The phlogopite products are used where a high heat resistance is desirable.

The cloth and tape are made by bonding a thin layer of mica splittings to a backing of cotton, silk, rayon or fiber-glass cloth with a shellac or gypal binder. Mica plate is made by spreading alternate layers of mica splittings and binder until the required thickness is obtained and then dried under heat and pressure to secure uniformity of thickness and density. The cloth and tape are thin and flexible materials with excellent insulating properties, which can be wound around coils of elec-

tric generators and motors. The plate is a hard, dense material, which can be milled to accurate dimensions, and by using a suitable binder it can be molded into three-dimensional forms. The greater part of built-up mica plate is used as insulation between the copper segments of electric generators and motors, as it wears down equally with copper. With the perfection of inorganic bonding compounds, increasing quantities of built-up mica plate are being substituted for sheet mica in the manufacture of heating elements for electric household appliances.

Phlogopite mica has a higher heat stability than muscovite, with about the same voltage breakdown. However, phlogopite has a higher power factor than muscovite and cannot be used as a dielectric in capacitors or in other applications requiring low power losses. The principal applications of phlogopite are as insulation for heating elements, electric soldering irons, military searchlights and as nose washers for aircraft spark plugs.

The best grades of expanded vermiculite weigh from 6 to 8 lb per cu ft. Low density, comparatively high refractoriness, low thermal conductivity, and freedom from deterioration make it an excellent thermal and acoustic insulator.

Scrap mica has no other use than as the raw material in the production of ground mica, which is prepared by both wet and dry grinding methods.

Wet-ground mica has its principal use in the paint industry. In the wallpaper trade, with suitable vehicles, it is used as a decorative ink. It is used as a filler for rubber and for painting the water bags used in vulcanizing rubber, as it prevents sticking and gives an excellent finish.

Dry-ground mica is used in large quantities for coating roofing materials. During the war it was used to surface a composition material for aircraft landing strips. Other uses are in coating fabrics to make them waterproof, as the base of paint for covering pipe lines, in oil-well muds, and in a bonded glass material of which the trade name is Mycalex.

PRODUCTION AND CONSUMPTION

The United States is the largest consumer⁷ of mica and, measured in terms of all classes of mica mined, is one of the world's largest producers. However, in terms of first-quality sheet mica, essential in the electrical industry, the United States, under the impetus of bonuses during the war, produced but 12 pct of its requirements of sheet mica in qualities of good stained or better. The greatest output from domestic mines of uncut mica larger than punch and circle was in 1943, when the production of all classes of mica totaled 47,861 tons, of which uncut sheet larger than punch and circle comprised 0.79 pct; punch and circle, 2.81 pct, and scrap, 96.40 pct.

Mica splittings are almost all imported from India, although serious efforts have been made in this country to produce them by mechanical and hand methods. The greatest consumption of mica splittings in the United States was in 1944, a total of 4400 tons, of which 29 tons was of domestic production.

It is difficult to make comparative figures of the world's productions of mica because of the different methods of preparation, qualifi-

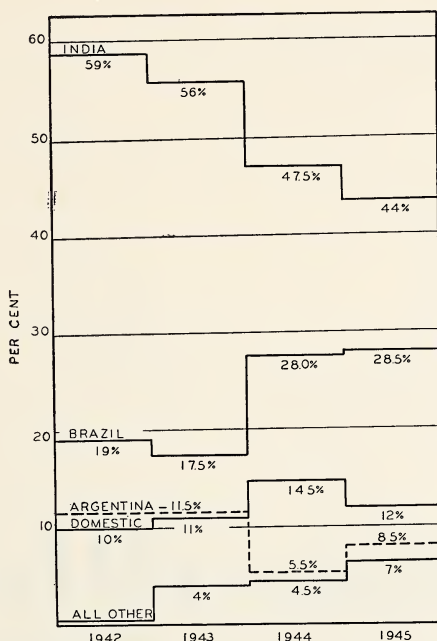


FIG 1—IMPORTS AND DOMESTIC PRODUCTION OF BLOCK MICA OF GOOD STRAINED OR BETTER QUALITIES, 1942-1945.

The percentages in the figure relate to definite quantities received from the countries named. The original statistics were compiled by the Mica-Graphite Division of the War Production Board and were incorporated in an unpublished report. The percentages are informative in that they show the position of the United States with respect to its ability to supply its own mica of strategic qualities. As the WPB was discontinued in 1945, later figures are not available on the same basis.

cation, and grading in the various producing countries. Nearly all India mica is prepared as full-trimmed whereas in the United States it is thumb-trimmed, half-trimmed, three-quarter trimmed, and full-trimmed. It was only during the period 1942 to 1945, when the Government controlled the production of mica, that American producers met the world standard of specifications. Since 1945, most of the domestic sheet produced has been of the half-trim classification, suitable only for household appliances, toasters, and similar articles.

Fig 1 summarizes the position with reference to imports of block

mica of good stained or better quality and domestic production of the same varieties.

The increasing importance of mica in our economy is graphically illustrated in Fig 2, which summarizes the situation with respect to imports of block mica, splittings, and domestic production of sheet and punch.

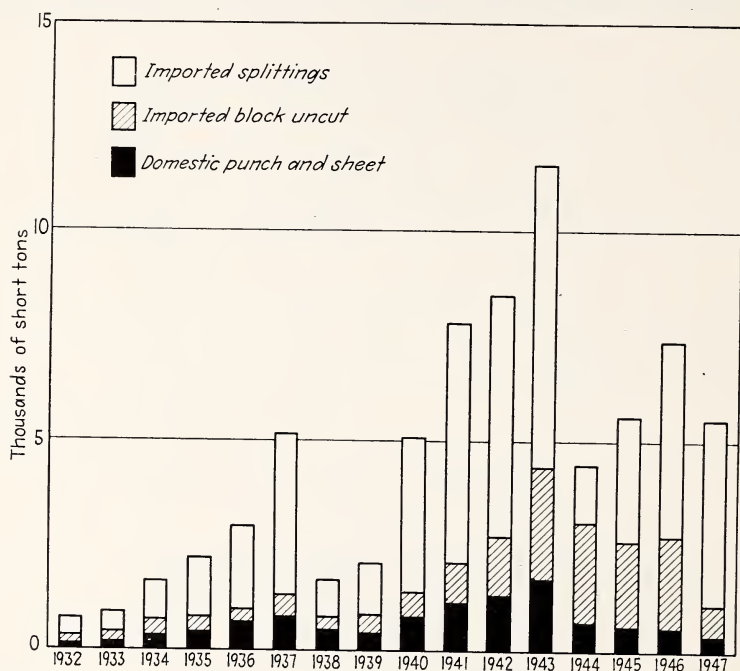


FIG 2—BLOCK MICA AND SPLITTINGS IMPORTED FOR CONSUMPTION IN THE UNITED STATES AND SALES OF DOMESTIC PUNCH AND SHEET, 1932-1947.

The growth of the ground-mica industries from 1923 to 1947 is illustrated in Fig 3, from which it can be noted that the greater part of the production came from domestic sources. In 1946, the uses by percentages were as follows: roofing, 48; paint, 23; rubber, 8; wallpaper, 5; plastics, 1; all other, 15. The production of 62,113 tons in 1946 is an all-time high.

PREPARATION AND QUALIFICATION

The crude mica crystals or "books" are first cobbled to remove the quartz and other materials adhering to the edges and then split with a knife into sheets of random thicknesses from a minimum of 0.008 in. up to 0.125 in. These sheets are then trimmed to remove edge imperfections and are known as the block mica of commerce. Trimming mica requires a high degree of skill with a knife, in order to remove cracks and other imperfections and at the same time accomplish the

best saving of usable mica. The India workmen are past masters in this trade. The sheets are trimmed with a beveled edge, in order to facilitate splitting into thinner sheets and films. In India, all mica is full-trimmed—that is, all imperfections have been removed from the edges—whereas in the United States several methods of preparation are in vogue: thumb-trim, whereby the most obvious defects are broken off

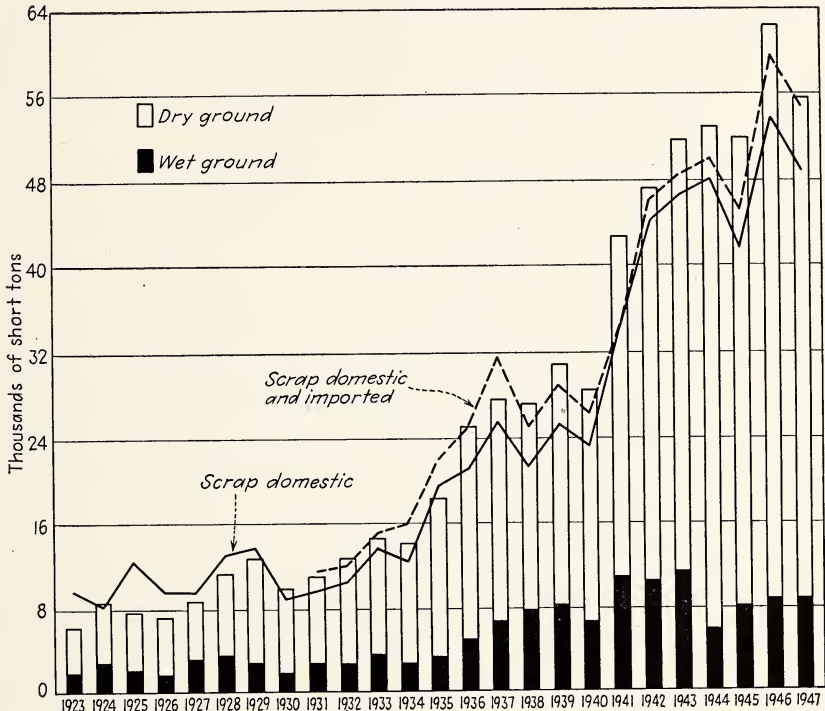


FIG 3—SCRAP AND GROUND MICA SOLD IN THE UNITED STATES, 1923-1947.

by hand; half-trim, in which all imperfection on two adjacent edges have been removed with a knife; three-quarter trim, in which the imperfections have been cut from three sides; and full-trim, corresponding to the India preparation. Consumers prefer part-trimmed Brazilian mica for the manufacture of radio-tube bridges and spacers and for electric-toaster and iron elements. The part-trimmed small mica gives the press operator more to hold to in punching the small radio-tube parts and the extra area permits the fabricator to get a larger pattern in punching the toaster and iron elements. The thinner residues of mica processing are known as scalings, cleanings, and chillas.

Mica film consists of irregular shaped pieces with the contour of the full-trimmed block from which they are split. The films are prepared to meet specifications of thickness usually in the order of 0.00125

to 0.002 in., 0.002 to 0.003 in., and 0.003 to 0.004 in., with a tolerance of 0.00025 in. The gauging into 0.00025-in. ranges is done in the United States. Indian splitters gauge by feel only and 0.001-in. ranges are about the best they can accomplish. Films are generally made of good-stained qualities of mica.

Mica splittings are thin pieces of mica of irregular shapes, which should not be more than 0.0012 in. thick and are preferred in thicknesses of from 0.0007 to 0.001 in. They are split from the lower qualities of block mica. Splittings are prepared as bookform, loose dust, pan packed, and loose. Bookform is made by carefully stacking the splittings from each piece of block mica so that the form of each original block is maintained. The splittings in the books are dusted with ground mica, which permits them to be readily separated. Small quantities of ground mica are scattered between layers of loose-form splittings to prevent them from adhering to each other. The grades (sizes) are confined to No. 4 and smaller. Both muscovite and phlogopite splittings are made in the same manner.

Sorting mica for quality and size is a costly hand operation and requires skilled workers. On account of the high cost of labor, it is not the usual practice in the United States to qualify mica according to world standards. The early production of mica in the United States was principally used for stove windows and accordingly sizes—i.e., “grades”—were expressed in inches. When the Government in 1942 undertook the production of mica, it introduced the world standards of qualifying and grading that had long been established in India.

The qualification of muscovite mica is made by visual inspection, the first test being the differentiation of color, ruby or green, with the varying shades of each. These two qualities are then classified as: (1) clear and slightly stained, (2) fair stained, (3) good stained, (4) stained, (5) heavy stained, (6) black stained.

Physical imperfections in muscovite influencing its classification are: air inclusions, waviness, mineral inclusions (magnetite, garnet, and others), “A” structure, pinholes, flexibility in thin films, “wedge,” “ruled,” and “tanglefoot,” which when present makes it difficult and in cases impossible to split the mica crystal into thin films.

Muscovite sheet mica is further classified into “grades” (meaning size, not quality) based on the rectangular area, free from cracks or other defects, which may be cut from each piece in the grade.

The grades generally recognized as world standards and the United States classification for the corresponding approximate sizes are as shown in Table 1.

In domestic grading, the smallest size, “punch,” is untrimmed mica large enough to yield a 1½-in. circle; the next size, “circle,” is untrimmed sheet that will yield disks up to 2 in.

The quality of phlogopite mica is determined by its resistance to

TABLE 1—*Grades of Mica*

No.	India Grading (Usable Area Based on Rectangular Sizes), Square Inches	United States Grading (Approximate Corre- sponding Sizes), Inches
6.....	1-2.5	Punch
5½.....	2.5-3	Punch
5.....	3-6	2 × 2 and 1.5 × 2
4.....	6-10	2 × 3 and 3 × 3
3.....	10-15	3 × 4
2.....	15-24	3 × 5
1.....	24-36	4 × 6
A1 or special.....	36-48	5 × 8
Extra special.....	48-64	6 × 8
Extra extra special.....	64-80	8 × 8
Over extra extra special.....	80-100	8 × 10

heat. The higher heat-resisting phlogopite is known as "Sparkplug" quality. The grading of phlogopite follows the standards for muscovite but seldom is found in the larger sizes.

Clear ruby India muscovite has long been the world's standard of quality. It was believed to be indispensable for use in the higher types of electrical equipment and green muscovite was not an acceptable substitute.

The U. S. Bureau of Mines and the National Bureau of Standards collaborated in a study of ruby and green muscovites from the mica-producing countries of the world, a report⁹ of which was issued in 1935. The conclusions drawn from the tests made by the Bureau of Standards are that there are no notable differences in any of the more important physical properties of domestic and foreign micas. Their dielectric strength, change on heating, and power factors are virtually identical. Other properties, such as flexibility and hardness, may be duplicated in comparable qualities. The preference of the consumer for India mica is due to its more careful preparation and grading, with consequent lower losses in the manufacture of finished products.

In 1940, the estimated requirement of first-quality mica indicated that the world's supply could not meet the demand, so the United States Government took steps for conservation by means of the allocation of existing stocks, downgrading by the use of lower qualities and the development of substitutes. Research was authorized to determine the relative values of ruby versus green mica, as well as the influence of staining on its electrical characteristics. Because of the lack of experienced workers on mica and the need for a rapid means of quality determination, the Government authorized a study of this problem.

The Bell Telephone Laboratories⁵ produced two portable battery-operated sets: (1) a spark-coil set for locating pinholes and conducting

particles in block mica, and (2) a direct-reading test set, operating at a frequency of one megacycle, for determining the dielectric strength.

The greatest use of fair stained and good stained mica is in capacitors. During and after World War II, stained quality mica was generally used for radio tubes and only limited quantities of good stained quality were used for this purpose.

Capacitors were made from mica qualified by the Bell test sets and rated against capacitors made of India ruby as the standard. It was found that tested green mica when used in capacitors gave results equal to those of ruby mica but that the losses in making mica film were greater for green mica than for ruby. Satisfactory capacitors were made from stained and spotted micas, qualified by the test sets, not considered useful for this purpose by visual qualification.⁵

Ground mica is made from scrap and is prepared by both dry and wet methods. For dry grinding, rotary driers are commonly used to expel excess moisture before grinding in high-speed hammer mills or pulverizers of the disintegrator type. Rotary and vibrating screens are used for sizing.

Wet grinding is done in chaser mills, consisting of annular wood or steel pans in which wood rollers rotating on a horizontal shaft revolve around a central shaft. The bottoms of the pans and the rollers are made of end-grain wood blocks. Wet grinding is a batch process and to complete a one-ton charge requires from 4 to 8 hr. Grinding is commenced dry and water is added gradually to form a thick paste. Heat is generated in grinding and careful adjustment of the water is required to prevent the mica from "burning." Too much water precludes proper grinding; too little allows the mica to burn and lose its sheen.

The ground charge is sluiced into wooden launders, where the sands and coarse mica settle. The overflow runs to settling vats, where the fine mica settles and the water is siphoned off. The mica sludge is dried on steam tables and then run over a vibrating screen to remove the plus 80-mesh. The undersize goes to bolting machines and is sized according to specifications. High-grade wet-ground mica specifications require 99.5 pct through 80-mesh and 88 pct through 325-mesh.

SUBSTITUTES

Research has been carried on for many years in an effort to find an acceptable substitute for mica. Materials made of paper, silk, vulcanized fibers, and asbestos, when impregnated with synthetic resins, oil, paraffin or asphalt, can be used in low-potential electrical equipment. The great demand for mica in 1940 gave impetus to the search for suitable materials that could be used instead of mica in the higher types of electrical equipment. Many investigations were conducted under both private and government auspices.

The earliest and possibly the most important saving of mica resulted from the development of ceramic plugs to replace mica spark plugs in aircraft motors, which were adopted by the Army in 1942 and later by the Navy. The high dielectric constants, controllable temperature coefficients and other unique properties of ceramics, permit their use in capacitors and make them more than a substitute for mica in many applications. Glass capacitors were approved for use by the Navy.

Paper, impregnated with synthetic resins and polymerized, has excellent dielectric properties for certain types of capacitors in which it finds its chief use. Lectrofilm, a paper impregnated with polyvinyl carbazole, and Diaplex, manufactured from bentonite clays and resin, have some applications but are high-cost products.

A report¹¹ indicates that Germany successfully produced phlogopite mica synthetically on a laboratory scale but was unsuccessful in creating muscovite. The report states further that, in attempts at mass production, the costs were from 10 to 20 times that of the natural product. The Germans also produced a synthetic resin bearing the trade name Luvican, which was used primarily for high-frequency insulation. Its application was limited on account of brittleness.

In 1946, the United States War Department awarded a contract to the Colorado School of Mines for research and development of a method for the production of synthetic mica.

Small crystals of synthetic mica are now being produced by melting in a special furnace carefully measured quantities of finely ground feldspar, magnesium oxide, and magnesium fluoride to temperatures up to 2700°F. Upon cooling, mica crystals form, which thus far have been small. The immediate problems are suitable containers for the melt and a controlled means of cooling, so as to produce crystals at least 2 in. square.

MARKETING

The marketing of mica is a complicated process, as the material usually passes through many hands before reaching the consumer. The greater part of production comes from small mines, which do not have facilities other than for cobbing the crude mica, books, which usually are sold to local buyers. Some buyers have a central shop, where the mica is split, trimmed, qualified, and graded to specifications.

Ground mica, being a bulk commodity produced as a finished product, is usually sold direct to the consumer.

PRICES

Trade statistics are not indexes of mica prices, owing to the difficulty of segregating the many qualities and grades. There are practically no standard quotations and purchases usually are made by negotiation between middlemen and the consumers. Formerly, London was the principal clearing house for India mica and continues to be the head-

quarters for sales on the Continent. However, nearly all India mica for the United States is now shipped direct from India. Most of Madagascar phlogopite mica is directly imported into the United States, only occasional lots coming from London or Marseilles.

During World War II, mica prices were controlled by the Combined Raw Materials Board, composed of representatives of the British Raw Materials Mission and the United States Procurement Agencies. Despite rigid conservation measures, the United States Procurement Agencies, in order to stimulate domestic production, rapidly increased the price of $1\frac{1}{2}$ in. by 2 in. No. 1 quality, full-trimmed muscovite from \$1.54 per pound in 1942 to \$8 per pound in 1944. During the same period, the resale prices for domestic sheet mica were based upon those paid by the United States Government for mica from foreign countries, plus import duty and an allowance of not less than 10 pct to cover handling charges. The wartime price schedule for strategic grades set by the Government was terminated Nov. 30, 1945. Thereafter, mica was bought and sold on the open market. Prices for domestic mica rapidly declined, owing, in the main, to its poor preparation.

The *Engineering and Mining Journal* Metals and Mineral Markets quotations for mica from North Carolina on March 4, 1948, are as follows:

CLEAR ONE-HALF		CLEAR ONE-HALF	
TRIM	PER POUND	TRIM	PER POUND
$1\frac{1}{2} \times 2$ in.	\$0.60 to \$0.65	3×4 in.	\$2.25
2×2 in.	0.95 to 1.00	3×5 in.	3.00
2×3 in.	1.35	4×6 in.	4.00
3×3 in.	1.80	6×8 in.	6.00

Stained or "electric" sheet mica is sold at prices 10 to 15 pct lower than for clear sheet.

North Carolina, wet-ground, \$110 to \$155 per ton, dependent on fineness and quantity; dry-ground, \$40 to \$80; scrap, \$25 to \$32, depending on quality.

Importers' quotations, March 1948, for India mica duty paid f.o.b. New York are listed in Table 2.

MINING METHODS

In general, the methods of mining mica may be described as primitive, for most mines are operated with a minimum of mechanical equipment and financial investment. The occurrence of mica in irregular pegmatites, and the spotty distribution of mica in these dikes, precludes their development in a systematic manner. Most of the smaller mica mines are operated as open pits, which are abandoned when the water level is reached. For hoisting, windlasses or stiff-leg derricks are in use, hand operated or by gasoline engines. Where prospecting and initial mining operations indicate the possibility of substantial quantities of

TABLE 2—*Importers' Quotations for India Mica, March 1948*
DUTY PAID F.O.B. NEW YORK

Grade	Prices, per Pound		
	Clear and Slightly Stained	Fair Stained	Good Stained
No. 1	\$24.98	\$18.18	\$13.31
No. 2	21.33	13.61	11.41
No. 3	18.48	12.66	10.70
No. 4	15.14	11.05	8.80
No. 5	10.58	7.04	5.26
No. 5½	5.87	5.24	4.09
No. 6	2.90	2.30	1.96

mica, vertical shafts are sunk in the wall rock and crosscuts are driven to the pegmatite. Such shafts usually are equipped with headframes, pumps, and hoists.

A prevalent method of entry is an incline equipped with track and cars. Where the terrain permits, the deposits are opened by adits, which follow the mica throughout its irregular course. Crosscuts to the deposits are the exception, owing to their initial cost before production begins.

Systematic stoping is generally impossible, owing to the nature of the mica occurrence, and the workings are therefore very irregular. The mica is recovered by breast or underhand stoping, for mica miners as a rule are averse to stoping overhead. When the rock is broken, it is hand-sorted, the mica books are placed in either sacks or boxes and sent to the cobbing house. As much of the waste as possible is left in the working and the remainder is transported to the surface. If mica is a by-product of feldspar mining, all the muck may be taken to the surface, where any mica not recovered in the mine may be sorted from the feldspar.

Fortunately, the ground usually stands well and little timber is required, but when necessary it is used as sparingly as possible on account of the expense.

In mining mica, care must be taken not to drill through or place powder charges in the mica pockets; these pockets, as far as possible, should be removed by mining around them. Light charges of 40 pct dynamite are used, so that the mica may not be damaged.

COSTS

Data on the quantities of mica produced per ton of rock mined are limited. In the North Carolina area, reports² show the average returns from 34 mines as 6 lb of mica; 10 mines, 16 lb; 18 mines, 27 lb per ton of rock broken.

The reported recovery from the New England³ states is an average of 28 lb of run-of-mine mica produced per ton of rock broken.

The approximate qualities and sizes of full-trimmed mica obtained from the run-of-mine crude is as follows:

	GOOD STAINED OR BETTER	Pct
$1\frac{1}{2} \times 2$ in. and larger		3.0
1×1 and $1\frac{1}{4} \times 1\frac{1}{4}$ inch		4.0
Washer		15.0
Scrap		78.0

The cost of mining mica is as variable as the nature of its occurrence. In large pegmatites, which permit of mining by opencut methods, the cost of mining ranges from \$0.50 to \$2 per ton; mining large pegmatites, underground, \$1.50 to \$3; narrow, steep-dipping pegmatites, \$2 to \$6; narrow, low-dipping deposits, \$3 to \$8 per ton; soft wet pegmatites \$4 to \$12. The average wage for mica miners was \$0.65 per hour.

The cost of preparation is extremely variable, being dependent upon the quality and size of the mica sheet and the skill of the operator.

The average cost of full-trimmed mica, including all sizes (No. 6 and up) at Spruce Pine, North Carolina, was \$0.90 per pound in 1944, with labor at \$0.40 per hour.

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CHAPTER 27

MINERAL FILLERS

BY ARTHUR B. CUMMINS*

POWDERED nonmetallic minerals and rocks of many different types are used extensively in industry for incorporation in compositions and manufactured products. The term "mineral filler" is commonly employed to designate a material that is used for a specific purpose but not as an essential or reactive component. Such a definition is not without objections, and it is indeed difficult to define fillers in any fully satisfactory manner, since the term has come to have so many different meanings and to cover such a wide range of uses.

A filler is defined, for the purposes of this chapter, as a substantially inert material not specifically employed as a reactive or essential component, the primary function of which is to modify the properties or processing of a composition of matter or fabricated article. Emery¹ has emphasized that fillers change the properties of the product but are themselves unchanged in compounding or use. The term "filler" appears to be rather general when referring to usages in bituminous compositions, rubber, composition floorings, fertilizers, plastics, textile finishes, and some others. In paper manufacture, in the paint industry and with insecticides, other terms are frequently employed, as is indicated hereinafter. By placing emphasis on the function of the material used in modifying the properties of the composition or article, it is believed that a more useful classification of filler products and their applications may be derived.

FUNCTIONS OF MINERAL FILLERS

All of the manifold functions of mineral fillers cannot be listed in a summary review. A survey of the uses for these materials, however, shows that in nearly all cases the powders are employed to modify the properties of a composition of matter or those of a fabricated article, or to perform some useful function in the manufacture of either. A generalized list of these useful functions may be given as follows:

1. *To Modify Optical Properties*

- Color
- Surface texture
- Opacity
- Brightness and gloss (as in paper and plastics)
- Flatness (as in lacquers and paints)

* Research Center, Johns-Manville Corporation, Finderne, New Jersey.

2. To Modify Physical Properties

- Change density (increase weight or bulk)
- Increase viscosity (raise melting or softening points, increase "plastic range")
- Increase strength (tensile, transverse, impact, crushing)
- Improve resistance to abrasion
- Increase toughness (resistance to pull, tear, shear, or distortion)
- Modify shrinkage and minimize cracking
- Increase hardness
- Improve heat and fire resistance
- Improve electrical resistance

3. To Modify Chemical Properties

- Improve chemical resistance
- Increase weather resistance

4. To Fill Voids

- In fibrous, felted and woven materials
- In surfaces
- As loose fill
- In molded or formed parts

5. To Modify Working Characteristics

- Mixability
- Lubrication
- Facilitate distribution

6. Primarily for Effect on Other Components of a Composition

- Dilution of essential components
- Maintain balance of properties in a mixture
- To obtain a definite composition
- Extend activity of a component
- Prevent caking or settling out
- Promote stability

7. Miscellaneous

- Lower cost

Filler materials fulfill these functions in varying degrees, depending upon the properties of the mineral powders, the compositions to which they may be added, methods of fabrication, and other factors. Consideration of the physical characteristics of mineral products is essential for an understanding of their effects when used as fillers.

PROPERTIES

The properties of milled mineral products that are of interest for their use as fillers are of two types: (1) those inherent in the individual particles themselves; and (2) those associated with masses of particles. These properties may be considered as intrinsic or fundamental, on the one hand, and as secondary (or mass) properties, on the other. Both are important, since the judicious selection of fillers for particular applications depends upon the balance and coordination of these properties with those of the composition into which the fillers are incorporated. Numerous properties of technical significance for particular applications are not included in the listing below, but such properties are usually related to two or more of the primary or secondary properties given:

Primary

Chemical composition (determines reactivity, solubility, pH, etc.)
 Specific gravity (particle or solid density)
 Refractive index
 Hardness
 Particle shape
 Surface properties (specific surface, electrical charge, adsorptive characteristics, surface texture)
 Color
 Thermal properties (specific heat, coefficient of expansion, melting point, decomposition temperature, conductivity, etc.)
 Microscopic and amicroscopic porosity
 Wettability

Secondary

(Variable with different conditions of preparations, packing and use)
 Particle size distribution (fineness modulus)
 Voids and pore openings
 Permeability (of packed filler)
 Liquid absorptive capacity
 Bulk density (loose, packed, wet, compressed, etc.)
 Abrasiveness
 Settling and sedimentation behavior
 Dispersibility or mixability
 Rheological characteristics (plasticity, etc.)
 Grittiness (presence of minor amount of oversize particle aggregates)

Some properties of the more important fillers are given in Table 1. The chemical composition of fillers ordinarily is less important than their physical properties, yet there are cases wherein composition is all important, since it determines solubility, reactivity, and other properties that may be critical.

The fundamental properties of particles such as specific gravity, refractive index, hardness and thermal properties, can be modified little if at all by milling and classification. Heat-treatments, however, may alter such properties to an important extent. Particle shape and surface characteristics are dependent somewhat on fineness and method of preparation but are mostly inherent in the natural mineral or rock itself. Fineness and particle size and all of the secondary characteristics are influenced greatly by the degree of milling and treatment during manufacture.

Fineness and particle-size data are not included in Table 1, since filler products may be supplied for various purposes in sizes ranging from macroscopic aggregates ($\frac{1}{8}$ in. or larger) down to extremely finely ground and classified materials of one micron size or smaller. Most commonly, however, mineral fillers are supplied as commercial 100-mesh to 325-mesh grades. Sieve or screen analyses are satisfactory for the coarser grades or for determining the percentage of "oversize" particles, which are generally considered as "grit" in the finer filler products. The particle-size distribution of subsieve particles is necessary to establish the "fineness," and in general, the utility of a material for many filler uses. The expression of particle size, however, must be defined in definite terms; such as, by weight, surface or frequency of particles. Complete distribution curves are necessary to indicate the true fineness of a product.

TABLE 1—*Properties of Important Fillers*

Class	Name	Nature	Approximate Chemical Composition
Asbestos	Chrysotile (7D Classif.)	Fibrous hydrated magnesium silicate	$3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
	Asbestic fines (floats)	Mostly serpentine dust with fine chrysotile	$3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
	Amphibole (anthophyllite)	Magnesium silicate with some iron	$(\text{Mg}, \text{Fe})\text{SiO}_3$
Barium sulphate	Barite	Barium sulphate	BaSO_4
	Precipitated BaSO_4 (blanc fixe)	Barium sulphate	BaSO_4
Carbon	Carbon black	Fine carbon from incomplete combustion of natural gas	Fixed carbon, 85–96 pct
Clays	Kaolin (China clay)	Essentially kaolinite	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$
	Bentonite	Primarily montmorillonite	$(\text{Mg}, \text{Ca})\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 \cdot n\text{H}_2\text{O}$
	Fuller's earth	Attapulgite and montmorillonite	Same
Micas	Muscovite	White mica	$\text{H}_2\text{KAl}_3(\text{SiO}_4)_3$
	Phlogopite	Amber mica	$(\text{H}, \text{K}, \text{Mg}, \text{F})_2\text{Mg}_3\text{Al}(\text{SiO}_4)_3$
	Vermiculite	Altered biotite	$(\text{OH})_2(\text{Mg}, \text{Fe})_3(\text{Si}, \text{Al}, \text{Fe})_4\text{O}_{10} \cdot 4\text{H}_2\text{O}$
Carbonates	Limestone (ground limestone, marble dust and chalk)	Calcium carbonate (with minor content MgCO_3)	CaCO_3
	Dolomite	Calcium magnesium carbonate	$\text{CaMg}(\text{CO}_3)_2$
	Magnesite	Magnesium carbonate	MgCO_3
	Precipitated CaCO_3 (whiting)	Chemically precipitated	CaCO_3
Talc	Magnesia talcs	Hydrous magnesium silicate	$\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$
	Pyrophyllite	Hydrous aluminum silicate	$\text{H}_2\text{Al}_2(\text{SiO}_3)_4$
Crystalline silicas	Crystalline quartz, ground sand and sandstone	Silica	SiO_2
	Microcrystalline tripoli	"Soft" silica	SiO_2
Diatomite	Natural	Opaline silica of diatom origin	$\text{SiO}_2 \cdot x\text{H}_2\text{O}$
	Processed	Same, usually calcined anhydrous	SiO_2
Limes	Hydrated lime	Calcium hydrate	$\text{Ca}(\text{OH})_2$
	Dolime	Calcium and magnesium hydrate	$\text{Ca}(\text{OH})_2 \cdot \text{Mg}(\text{OH})_2$
	Magnesium oxide	Magnesium oxide	MgO
Cement	Portland	Hydraulic cement from calcination of lime, clay, etc.	Essentially mixture of calcium silicates and aluminates
Calcium sulphate	Gypsum	Hydrated calcium sulphate	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
	Precipitated CaSO_4	Anhydrous calcium sulphate	CaSO_4

TABLE 1—(Continued)

Class	Name	Nature	Approximate Chemical Composition
Volcanic ejecta	Volcanic ash (pumicite)	Alkaline aluminum silicate	Mostly like rhyolite
	Perlite (expanded)	Same	Same
Stone and rock dusts	Slate	Metamorphosed sedimentary rock	Mixture of mineral silicates
	Shale, rottenstone, trap rock, etc. Igneous rock (granite, etc.), marl, loess, etc.	Various rock types	Mostly mineral silicates
Pyrogenous products	Ground cinders, fly ash, powdered slags, brick dust, powdered glass, etc.	Mostly waste products from various industries	Silicate of variable composition

Table continued on page 572.

Various methods for testing particle size have now become rather well standardized and are adaptable for use in filler work. A distinction should be made between the apparent or agglomerate size distribution of a product and its ultimate size distribution, since many materials are comprised of minute masses or clusters of particles requiring some mechanical work to effect a separation of the component particles. Perhaps the most satisfactory technical distinction is to differentiate particle size before and after complete dispersion. The application in hand and the method of incorporating the filler determines which size distribution is of most significance for a given use. Surface properties are useful also and necessary for some purposes. While some mineral-filler industries have not yet adopted particle size and surface characteristics as the determining factor for control in manufacture, for specifications, etc., the consumer industries are adopting these more and more in research and in practice. Figs 1 to 6 are photomicrographs of different types of mineral fillers.

MATERIALS USED AS FILLERS

Most of the nonmetallic industrial minerals, and many powdered rock products, have been employed to some extent at different times for numerous filler uses. These usages vary periodically, depending on availabilities, costs, technologic trends and advancements, and other factors. However, for the major applications and for the more particular requirements at any given period, there are some general trends which serve to favor a more or less restricted group of filler products for each of the major consumer fields. This selection of materials is determined by the characteristics of the individual filler products, their effectiveness in fulfilling the primary function or functions for which they may be employed, and the cost after incorporation in the finished product.

TABLE 1—(Continued)

Class	Density		Hardness (Moh's Scale)	Refractive Index	Color	Particle Characteristics
	Specific Gravity	Bulk, Lb per Cu Ft				
Asbestos	2.54-2.59	10-14	4-5	1.55	Gray, greenish to whitish	30-40 pct fiber about $\frac{1}{16}$ in. length
	2.5-2.65	20-40	2.5-4	1.51-1.54	Gray	Variable and mostly elong- ated and irregular
	2.9-3.2	12-20	5.5-6.0	1.58-1.64	Gray, greenish tan, whitish	Coarsely fibrous
Barium sul- phate	4.3-4.6	80-100	2.5-3.5	1.64	Gray, tan to white	Relatively coarse par- ticles, roughly isometric
	4.1-4.4	30-40	3	1.64	White	Dispersed 0.1-5.0 μ
Carbon	1.7-1.8	10-15			Black	Microaggregates; ulti- mate particles 10-30 millimicrons
Clays	2.6	20-40	2-2.5	1.56-1.58	White, cream or gray	Flat, hexagonal plates and porous aggregates, 0.5-50 μ
	2.2-2.7	50-60	1.5	1.50	Light tan or cream	Porous microaggregates, irregular, more or less rounded; ultimate thin plates
	2.2-2.6	27-38	4	1.50	Light buff, gray cream, grayish white	Spicular-granular; ulti- mate-fibrous
Micas	2.7-3.0	12-20	2-2.5	1.59	Whitish to white	Thin plates, micaceous
	2.9	12-20	2-3	1.6	Amber	Thin plates, micaceous
	2.3	5-15	1.5	1.56	Tan or golden	Thin plates, micaceous
Carbonates	2.7	40-60	3	1.63-1.66	Whitish to white	Variable sized particles; ultimate rhombs
	2.85		3.5-4	1.68	Whitish, gray to white	Like limestone
	3.0-3.1		3.5-4	1.70	Gray, pink, white	Like limestone
	2.6	30-45	3	1.65	White	Fine particles; rounded and aggregates
Talc	2.7-3.1	26-60	1-1.5	1.57-1.59	Gray greenish to nearly white	Flake talc; lamellar grains approx. equidimen- sional. Fibrous talc; 10 pct tremolite fibers or splinters
	2.7-2.85	25-30	1-2	1.59	Grayish, cream off- white	Flat platelike flakes
Crystalline silicas	2.65	50-80	7	1.54	White or colorless	Irregular, angular, sharp
	2.2-2.6	55	6.5-7	1.53	Rose or cream	Irregular, more or less rounded; microporous aggregates

TABLE 1—(Continued)

Class	Density		Hardness (Moh's Scale)	Refractive Index	Color	Particle Characteristics
	Specific Gravity	Bulk, Lb per Cu Ft				
Diatomite	2.0-2.2	6-20	5.5-6	1.42-1.45	Gray, cream to whitish	Diatomaceous
	2.15-2.35	8-15	6-6.5	1.44-1.49	Pink or white	Diatomaceous
Limes	2.2	25-45	2	1.57	White	Irregular edged and spongelike particles
	2.3	30-50	2-2.5	1.6	White	
	3.6	4-20	4-5	1.73	White	Fine irregular aggregates, ultimately cubical
Cement	2.9-3.15	90-100	5-6	1.72 (rough average)	Light to dark gray	Variable. Smooth rounded, angular, and flake particles
Calcium sulphate	2.3	25-40	1.5-2	1.52	White	Irregular, roughly isometric
	2.95		3-3.5	1.59	White	Fine elongated particles
Volcanic ejecta	2.2-2.63	40-50	5.0-6	1.49-1.50	Gray or pinkish	Irregular and cellular
		4-20	5.0	1.48-1.49	Gray to white	Minute expanded "glass" bubbles and fragments
Stone and rock dusts	2.8	40-50	4-6		Gray, green and other colors	Irregular, flat
	Variable	Variable	Variable	Variable	Various colors but not white	Variable
Pyrogenous products	Variable	30-80	Variable	Variable	Various colors, but rarely white	Variable

Table continued on page 574.

The more important mineral fillers include limestone and whiting, clays, crystalline silicas, talcs and pyrophyllite, micas, barite, diatomite, asbestos, carbon black, limes, cement, slate dust, ground rocks, earthy materials, and various types of pulverized waste materials such as slag or fly ash. Less important minerals used as fillers are tripoli, pumice, gypsum, bauxite, feldspars, phosphate rock, vermiculite, perlite and others. There are still other materials of less frequent use as fillers.

Some organic materials, such as wood flour, sawdust, fibers, cork, nut meal, are of great importance as fillers and are used extensively. These are of interest as competitive materials for mineral fillers and of still greater interest for uses in which organic and mineral fillers are used advantageously in combination.

The minerals listed in the foregoing paragraphs, their occurrences, methods of mining and beneficiation, political and commercial control, and other data, are considered separately in other chapters of this volume. Properties of particular interest for usage as fillers, together with

TABLE 1—(Continued)

Class	Reaction or pH	Solubility	Oil Absorption (Gardner-Coleman)	Refractoriness	Distinguishing or Characteristic Properties	Approximate Quantity Used for Filler Purposes, USA, Tons
Asbestos	8.3-8.5	Soluble in acids	60-90	Dehydrates 1500°F	Most fibrous of all mineral fillers	150,000 (1948 est.) Mostly Group 7
	8.3-8.5	Soluble in acids	40-60	Dehydrates 1500°F		
	8.0	Resistant to acids	100-160	High		Nominal
Barium sulphate	7	Insoluble	6-10	High	Heaviest density filler	50,000 (1945)
	8	Insoluble	10-20	High		30,000 (1945)
Carbon	Slightly acidic	Inert except in organic solvents	30-90	Low	Extreme fine particle size. Only black filler	423,000 (1945)
Clays	4.5-7	Low	25-50	High	Soft, fine particles	960,000 (1946)
	6.2-9.0	Low	20-30	High	Soft, fine particles	12,000
	7.5-8.2	Low	30	High	Soft, fine particles	6,000
Micas	7.4	Low	40-50	High	Flat micaceous structure characteristic	62,113 (1946)
		Low		High		
		Low		High		
Carbonates	7.8-8.5	Soluble in acids	12-30	Decomposes at high temperatures	Soft, slightly alkaline. Relatively cheap filler	1,400,000
		Slowly affected by acids		Decomposes at high temperatures	Like limestone	Not available. Less than limestone
				Decomposes at high temperatures	More inert than limestone	Small
	8.3-9.6	Soluble in acids	25-60	Decomposes at high temperatures	Generally white and finer than limestone	Not available
Talc	8.5-9.4	Low	25-50	High	Smooth, platy structure	360,000 (approx.) 80 pct (1946) talc; 20 pct pyrophyllite
	6-8	Low	25-50	High	Like talc, but more inert	
Crystalline silicas	7	Insoluble	20-30	Very high	Hard, sharp particles and very inert	30,000 (est.), 1946
	6-7	Insoluble	30-55	Very high	Unique micro-porous structure	4,500 (1946)

TABLE 1—(Continued)

Class	Reaction or pH	Solubility	Oil Absorption (Gardner-Coleman)	Refractoriness	Distinguishing or Characteristic Properties	Approximate Quantity Used for Filler Purposes, USA, Tons
Diatomite	6-7	Insoluble	100-250	High	Unique diatom structure; high absorption	80,000 (1947)
	6-8.5	Insoluble	100-250	High		
Limes	11.3-12.5	Somewhat soluble in water	40-80	Very high	Definitely alkaline	
			35-70	Very high		
			200-300	Very high		
Cement	11.0-12.6	Sparingly soluble in water	20	Breaks down 1200°-1500°F	Alkaline; Cheap. Hydrates with water	Not available. Considerable quantities in asphalt surfacings
Calcium sulphate	6.5-7	Somewhat soluble in water	17-25	Loses H ₂ O low temperature	Most soluble of common fillers	35,000 (1946)
	8.5		50	High		Not available
Volcanic ejecta	7-9	Very slightly soluble	30-40	High	Irregular and abrasive	Small
	9		50-275	High	Porous and light weight	500 (est. 1947)
Stone and rock dusts	6-8		20-25		Colored, cheap	Total tonnage slate granules and flour, 482, 230 (1945) (not all for fillers). Ton-nage of other rock dusts not available but very large.
		Generally insoluble	Variable	High	Cheap and readily available	
Pyrogenous products	6-8.5	Generally insoluble	Variable	Generally high	Cheap and readily available	Filler tonnages un-available but are large

Table continued on page 576.

some estimates of tonnages and prices, are given in Table 1, which also indicates the major fields in which they are used. Data included in the table should be regarded as suggestive and generalized, rather than as positive. Chemical formulas and physical properties for the most part are for theoretical and pure materials. Tonnages and prices are averages, and these vary widely with economic cycles. Figures given are for recent years of great business activity. Future conditions probably will change these figures upward and downward radically. There is a wide spread in the prices for the different grades of some fillers. Thus, talc for some filler uses is sold for less than one fourth the cost of other more selected grades required for other uses. The listing of principal uses as fillers is for the years 1945 to 1948. There may be substantial changes in future years.

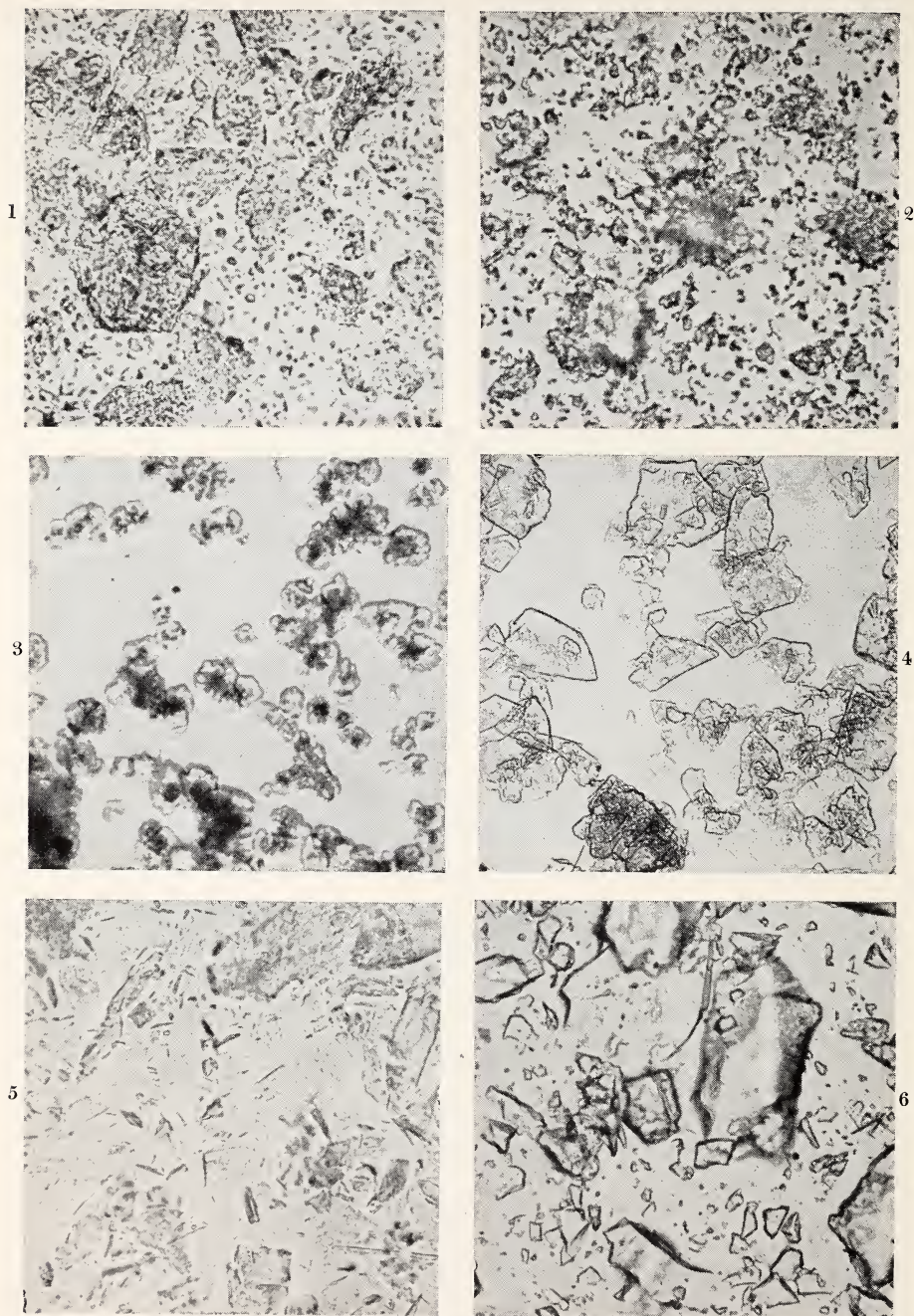
Mineral fillers may be modified to greater or less degree by methods directed toward coating the surfaces of the particles. Organic coatings, particularly stearic acid and resinous compounds, are employed success-

TABLE 1—(Continued)

Class	Approximate Price per Ton (Carloads at Mines)	Relative Abundance in USA	Principal Uses as Filler	Remarks
Asbestos	\$40-\$50 (1948)	Totally inadequate	Floor tile, plastics, welding rods and miscellaneous	Other uses, 1948 est. 200,000 tons (groups 4, 5 and 6); for asbestos-cement products: 130,000 tons (groups 3-7); for asbestos mill-boards, friction materials, pipe covering, roofing and black lines
	\$27 (1948)			
	\$10-\$40	Limited	Insulating compositions, battery boxes, plastics, paints, etc.	Relatively unimportant up to present
Barium sulphate	\$16 (1945) Bleached \$28 (1945)	Abundant	Paint, rubber, paper, plastics, oilcloth and linoleum, wallpaper, printing inks, textiles, leather	Other uses in 1945: oil-well drilling, 407,871 tons; chemicals and lithopone, 238,461 tons; glass mfg., 25,761 tons
	\$60-\$70 (1945)	Abundant		
Carbon	\$80 (1945)	Production exceeds use (important exports)	Rubber (85-90 pct of total), printing inks, paint, and miscellaneous.	Potential depends on natural gas
Clays	\$9-\$15; Spec. Grades, \$40	Abundant	Filler and coating for paper, rubber, linoleum, paints, textiles	Clays other than kaolin, bentonite and fuller's earth used for filler purposes in 1946 = 25,000 tons
	\$10-\$18 (1946)	Somewhat limited	Insecticides	Foundries, etc, 165,044 tons; drilling mud, 231,252; filtering and bleaching, 150,189; concrete admixture, etc., 1,227; other uses, 44,290
	\$7-\$12 (1946)	Abundant	Mostly insecticides; other misc. uses	Decolorizing oils, 230,080 tons; floor absorbent, 49,036; drilling mud, 9,776; other, 4,185
Micas	\$47.50 dry-ground; roofing grades, \$50; \$85-125 wet ground	Relatively limited	Roofings, paints, rubber, wallpaper, plastics and various misc. uses	White micas most generally used. Biotite and phlogopite each used to increasing extent. Expanded vermiculite as insulation used as loose fill in cements
		Adequate		
		Limited		Only small amount of vermiculite used as filler
Carbonates	\$4-\$30 special grades	Abundant	Asphalt surfacings, fertilizers, calcimine, oil paints, rubber, linoleum, paper, misc.	Asphalt, 455,360 tons; fertilizers, 401,160; limestone whiting, 343,220; misc. filler (not whiting sub.), 138,750; other uses in putties and chemical industries
	\$4-\$20	Abundant	As alternate for ground limestone	
	\$12-\$20 (crude)	Limited	Uses minor	
	\$16-\$100	Abundant	Paints, paper, rubber and misc.	

TABLE 1—(Continued)

Class	Approximate Price per Ton (Carloads at Mines)	Relative Abundance in USA	Principal Uses as Filler	Remarks
Talc	\$8-\$45 (1946)	Abundant	Paint, rubber, roofing, insecticides, paper, toilet preparations, asphalt, textiles, and many misc. uses	Steatite and pyrophyllite in ceramics (1946), 62,389 tons; foundry facings, 7045 tons; hard, soft, fibrous and flake varieties used as fillers; steatite and soapstone not important as fillers
	\$10-\$14 (1946)	Limited	Paper, rubber, battery boxes, insecticides, roofings, textiles, asphalt, etc.	
Crystalline silicas	\$4-\$16 \$4-\$12	Abundant Abundant	Cements and plasters, asphalt, paint, rubber and misc.	Major uses in ceramics, abrasives, and foundries (mold wash and parting).
	\$14-\$40 (1946)	Abundant	Paint. Used also in admixtures, ceramics and numerous misc. uses	Major use is as in abrasive and buffing compounds
Diatomite	\$20-\$120	Abundant	Paints, asphaltic compositions, plastic, pesticides, paper, rubber, etc.	
Limes	\$9-\$12	Abundant	Asphalt	
	\$8-\$12	Abundant	Asphalt	
	\$40-\$160	Limited	Neoprene	
Cement	\$12-\$15	Abundant	Asphalt	
Calcium sulphate	\$8-\$11	Abundant	Fertilizers, paint, paper, cloth, insecticides	Major uses as portland-cement retarder, land plaster, plasters and wallboard
	\$15-\$30	Abundant	Paper, textiles, insecticides	
Volcanic ejecta	\$14-\$20	Abundant	Soaps, insecticides, paint (traffic), plastics, absorbents, etc.	Major uses in cleansing and scouring compounds; also concrete admixtures and aggregates, stuccos and plasters
	\$30-\$40 (Processed)	Abundant	Filler uses undeveloped. Being considered for many usual applications	Expanded perlite advocated for building materials, plasters, etc.
Stone and rock dusts	Slate dust: \$6-\$10	Abundant	Slate flour used as filler in road asphalt surface mixtures, paints, roofing, mastics and linoleum	Slate granules used extensively for surfacing prepared roofing
	Rottenstone, \$25; other rock dusts, \$2-\$8		Asphaltic compositions of different kinds and for numerous cheap fillers	
Pyrogenous products	\$2-\$10	Abundant	Asphaltic compositions, paving, etc., in concretes and mortars and various low-cost fillers	



FIGS 1-6—PHOTOMICROGRAPHS OF MINERAL FILLERS.

1. Fuller's earth. $\times 250$. 3. Whiting. $\times 500$. 5. Talc. $\times 250$.
2. Tripoli. $\times 500$. 4. Mica. $\times 250$. 6. Quartz. $\times 250$.

fully for treating calcium carbonate fillers. These coatings usually are applied by dry methods. Thin films of calcium soap or resinate are formed on the surfaces and have extended the usefulness of whitening for many filler purposes. For use in rubber, the stearate coating is preferred, whereas for paints the resinate coating appears more advantageous. Clay, silicas and other mineral fillers may be surface-treated in similar manner.

MAJOR FIELDS OF USE FOR MINERAL FILLERS

The large filler-consuming industries, all of which take substantial tonnages, are bituminous compositions, paper, protective and decorative coatings, plastics and molded compositions, rubber, fertilizers and pesticides. Of somewhat less importance are textiles, floor coverings, cosmetics, light-weight compositions, welding rods, waxes, loose fills, stock feeds, and others. There are a considerable number of minor uses, some of which are of considerable technical importance and interest but which do not involve large tonnages. In addition, many usages and applications of industrial minerals are somewhat related to strict filler usages or may be borderline filler uses. Some of these involve considerable tonnages of mineral products, the preparation, testing, and marketing of which is much the same as for filler products. Examples of these are lubricants, antisticking agents, surface coatings, supports and carriers, mold washes and parting compounds, anticaking agents, absorbents, putties, components of abrasive compositions, soaps, insulations, cements, mortars and concretes, and conditioner for molding sands. Only brief discussion of the major uses can be given.

Bituminous Compositions

Mineral fillers are used extensively in paving mixtures, in surfacing for asphaltic concrete, for sheet roofing and shingles, bituminous cements, enamels and lacquers, floor tile, mastics, expansion joints, molded bituminous compositions such as battery boxes and for bulk revetments.

Fillers fulfill several important functions in bituminous compositions. Their effect is to increase the melting or softening points, increase viscosity, extend the "plastic range," increase hardness, increase stability, increase tensile strength, augment weather resistance and minimize checking and cracking.

Selection of fillers as to type and fineness is dependent upon the combination of properties desired, the nature of the bitumen mixture and economic considerations. In asphaltic paving mixtures and in the surfacing of asphaltic concrete, very large tonnages of ground limestone, other rock dusts, silicas, slate dust, portland cement and hydrated lime are used. Earthy materials, impure clays and loess are incorporated in

large volume for massive construction such as asphaltic mattresses for flood control. The improvement in the stability of the bituminous road and building construction is mainly due to the effect of the finely divided particles in increasing the viscosity of the bituminous binder.

Suitable grades of mineral fillers improve the weather resistance of all bituminous substances, which accounts for their extensive use in many types of surfacings, roofings, and other materials subjected to changes in weather. Minimizing of checking and cracking, hardening, increase in "plastic range," all contribute to better weather resistance. For surfacings, opaque or colored filler particles are preferred, since they reduce the deleterious effect of sunlight on the binder. Materials used most commonly for bituminous surfacings are pulverized sand, limestone, slate dust, clay, talc and rock dust.

For bituminous lacquers and enamels, increased hardness and melting points are most important. The more absorptive fillers—for instance, diatomaceous silica—are advantageously used here. For floor tile, expansion joints, bridge planking, mastics, and similar purposes, ground limestone, marble dust, ground serpentine rock, asbestic floats, and other fine fillers are used, generally in combination with pigments and fibrous materials. For molded asphaltic compositions, choice of fillers is somewhat more restricted; fibrous materials, cotton linters or amphibole asbestos are employed with finely divided minerals, principally pyrophyllite or diatomite.

A substantial amount of basic research work and practical studies on the use of fillers in bituminous compositions have been carried out in the more important fields of application—directed mostly to the grading and selection of fineness moduli and combination of properties best suited for a given purpose. References given hereinafter indicate the scope of more recent work. The third edition of Abraham's book on *Asphalts and Allied Substances*¹³ is comprehensive. A study on the use of fillers in road surfaces by Rigden¹⁸ is suggestive for most asphalt fillers.

Paper

The use of mineral fillers in paper manufacture is general, some being used in nearly all papers. "Coating" is the term employed for the application of a mixture of mineral-pigment adhesive to the surface of a sheet. When the mineral agents are added to the furnish (usually at the beater), they are considered to be fillers or loading materials. Fillers function in paper to fill voids between the fibrous particles. In this way they improve the printing quality by increasing opacity, improve the texture or "feel," impart a better finish on calendering and increase the weight of the finished sheet.

China clay and whiting (mostly precipitated type) are the two most widely employed paper fillers. Talc, calcium sulphates and barium

fillers are also used commonly. In recent years, there has been a large increase in the use of titanium oxide and zinc pigments, which are used advantageously in combination with mineral fillers for better quality of paper. Newer types of surface-treated whittings are accepted widely.

The effect of fillers on the color, opacity and brightness of paper is complex. The internal surface of the sheet is increased by the mineral particles of relatively high specific surface, and thus there is greater light scattering within the sheet. Exact relationships are dependent upon various factors such as the character and fineness of the particles, their refractive index and properties of the fibers. Studies by Gaegauf and Müller²² are helpful in explaining some of these relationships.

Protective and Decorative Coatings

Present-day formulation in paints, pigmented varnishes and lacquers recognizes an important relationship between the quality of the protective film structure and the pigment-vehicle system, wherein various nonmetallic mineral products play an important role. Bradley³² considers these materials as low-refractive-index (LRI) pigments. Their use is fully established for the best standards of manufacture. The more important materials of this class that are used in protective coatings are barium pigments (ground barite and blanc fixe), kaolin, whiting, talc, quartz, diatomite, mica, gypsum and some others to minor extent. The coarse particle size of pumice has a place as an ingredient for traffic paints. In water-base paints, calcimines, oleoresinous emulsion paints, casein paints, and others, LRI pigments largely replace the prime white pigments used in oil paints.

Mineral products have various functions in paints. A summary given by Harness³⁵ is:

1. To dilute primary pigment in the manufacture of inexpensive paints (barite, clay, sericite, whiting).
2. To facilitate suspension (mica, bentonite, kaolin, talc).
3. To increase resistance to moisture (mica, sericite).
4. To strengthen paint film (mica, sericite, talc, diatomite).
5. To give characteristic finish to flat paints and lusterless enamels (talc, kaolin, diatomite).
6. To thicken primers (kaolin).
7. To improve sanding properties (barite, quartz, diatomite).
8. To increase density of film (barite).
9. To aid working with brush (barite, diatomite).
10. To assist primers in filling pores (diatomite, talc).
11. To enhance wearing properties of paint films exposed to abrasion (diatomite, talc, quartz).

Rubber

In the compounding of rubber articles, there is a general distinction between reinforcing materials and loading materials, such as extenders and inert fillers, although there is no sharp distinction between these classes of compounds and full agreement does not exist among rubber technologists as to proper classification for some of the non-metallic minerals used in rubber compounding.

By far the most important reinforcing pigment for rubber is carbon black (channel process first and soft gas carbons second), which has pronounced effect in increasing the tensile strength, modulus and resistance to abrasion and tear of rubber.

The inert fillers used most widely are whiting, clays, talc, barite, slate flour, diatomaceous earth and mineral rubber. Mica, asbestos, dolomite, calcium sulphate, and some other minerals are used to a lesser extent. These materials improve the processing of some rubbers, improve certain specific physical properties, and lower compounding costs. With unvulcanized stocks, fillers have a favorable effect in calendering and tubing operations, tending to smooth out the stock in processing. In the use of mineral products to extend the volume of rubber without undue sacrifice of physical properties, the specific gravity of the filler is important, because volume rather than weight determines the cost. Powdered mineral products may be used more extensively with some of the synthetic elastomers than with rubber. Synthetic rubbers of the Buna N and Buna S types, neoprene, and butyl rubber may all be compounded with mineral fillers in combination with black or in non-black stocks. Light calcined magnesium oxide is considered to be an essential compounding ingredient for neoprene stocks. Precipitated hydrated calcium silicate has value for primary use as an extender pigment, particularly for white stocks.

European practice in the fabrication of rubber products appears to favor a broader use of mineral products and so-called inerts in rubber than does American practice. Sommerfeld³⁰ presented a useful discussion of mineral fillers in rubber compositions, with an attempt to explain their advantages theoretically. Lewis and Squires³ consider that in rubber compounding "the flow of the rubber around the ultimate particles of filler during incorporation on the mill tends to orient the molecular chains of the rubber parallel to the surfaces of the particles with which they are in immediate contract." Corollaries of this observation are that the size of filler particles must be small and generally more or less isotropic in shape, rather than fibrous or platy.

Plastics and Molded Compositions

Organic fillers, wood flour, cotton flocks, and similar materials are the common fillers for plastic moldings. Mineral fillers are used for

special purposes. Short-fiber asbestos and asbestos floats are employed for moldings that must have high heat resistance; mica for high electric strength; diatomite for surface finish, heat resistance and balance of other properties. These fillers all tend to reduce mold shrinkage and improve water resistance. Clay, gypsum, barite, slate, crystalline silicas and other fillers are used to minor extent. Asbestos, mica and diatomite are used frequently in combination with wood flour for thermosetting plastics.

For abrasion-resistant compositions of both the thermoplastic and thermosetting types, diatomite, clay and other fillers are advantageous. In material for making phonograph records, highly refined diatomite is employed for the higher priced records and clay, gypsum or other cheaper filler is used for the less expensive records.

Phenolic plastics perhaps use the largest amount of mineral fillers. This subject has been reviewed currently by Debing.⁴¹ He concludes . . . "the ideal filler has not been attained, since four different fillers are required to produce the range of properties needed by industry. However, in lieu of the ideal filler, if superior properties can be attained for specific end uses by special fillers without the sacrifice of other desirable characteristics, such fillers will be looked upon with favor." Debing indicates that about 63,000 tons of wood flour, 10,000 tons of asbestos and 3,500 tons of all other fillers were used in 1947 for phenolics.

Pesticides

The use of insecticide dusts and pesticide dusting powders generally has been increasing steadily. In the trade, mineral powders used in combination with active toxicants are usually referred to as diluents. These are necessary with expensive insecticides, to provide effective distribution of the poisonous principle, and in other cases to effect the necessary economy. Other functions of the diluent are to improve adherence to foliage, to control drifting, and in some cases to increase the lethal effect of the toxicant. Insecticide dusts are applied by hand and power-driven ground machines and by airplane and autogiro. Materials most commonly used are clays, talcs, fuller's earth, diatomite, gypsum, lime, and pyrophyllite.

Insecticides used with mineral dusts include cryolite, sulphur, nicotine, arsenates, basic copper sulphates, rotenone, pyrethum, DDT, benzene hexachloride, and some of the newer organic toxicants. Some of the considerations involved in insecticide dusting have been given by Moretti.⁵⁴ The New York Agricultural Insecticide and Fungicide Association has provided a compilation of data on commercial diluents and carriers.⁵⁸ Recent trends and reports on research work and field tests have been given by Turner⁵⁵⁻⁵⁷ and others.^{50,53} The use of inorganic dusts for the control of weevil growth in stored grains^{51,52} is of technical interest but legislative action apparently discourages this usage. The

use of mineral fillers in dusting powders for the control of animal parasites is important but is not a large tonnage outlet for the fillers. Ground pyrophyllite has been used most extensively for DDT louse powders.

Fertilizers

The practice of adding inert mineral matter to commercial fertilizers has been on the decrease for the past decade. However, more than 1,000,000 tons per annum has been employed in the recent years of high production for mixed fertilizers. "Sand," dolomite, limestone and gypsum are the major materials used. Small tonnages of peat and peanut-hull meal are employed. An important use for mineral powders, as well as for some other materials, in fertilizers is to prevent hard caking and to maintain drillability. Calcium cyanamid, neutral phosphate, processed tankage and some relatively inert organic materials, such as crop residues and peat, are employed for this purpose. Superphosphate has a definite tendency toward hard caking. Ammonium nitrate is treated with diatomaceous earth or kaolin to prevent hard caking. The purpose in the use of these materials has been primarily to adjust the ratio percentages of plant-food ingredients. Earth, ground cinders, ashes and other low-cost available materials are also employed and are usually included in the statistics as "sand." Crude phosphate rock is similarly used and has some value because of its P_2O_5 content. A significant trend in recent years has been the increased usage in mixed fertilizers of limestone and dolomite rather than sand and non-reactive silicate materials.

Mehring⁴⁶ has summarized the entire problem in the use of fillers in fertilizers. He defines a filler as any material added to fertilizers that contains little or no available nitrogen, phosphoric acid or potash. He discusses briefly the manufacture, sale and trends in formulations of mixed fertilizer with and without filler. The tendency, no doubt, is toward less usage of unnecessary filler and the encouragement of the purchase of fertilizers on a unit plant-food cost rather than on a price-per-ton basis. For many years, however, considerable tonnages of low-cost mineral materials will probably continue to go into many mixed fertilizers.

Textiles

In textile finishing, the sizing used for fabrics is frequently a mixture of starches or dextrans and a mineral filler such as clay, barite, steatite or gypsum. Glycerin, glucose and various hygroscopic salts are also employed. The size cements the fibers together, increasing the tensile strength, and improves resistance to soiling and provides a glossy finish. Fillers tend to fill voids between fibers, thus stiffening the fabric

by reducing flexing of the fibers. Cotton and the heavy fabrics, such as jute or canvas, are most frequently sized. Clark⁵⁹ has summarized textile fillers as follows:

"When used in cotton finishings, mineral fillers are applied to increase the weight, extend the fibers, and to close up the interstices between the yarns as well as to produce opacity or covering effect, the purpose of this being to simulate the appearance and weight of better fabrics . . . Consideration of physical rather than of chemical properties generally is the basis of the selection (of fillers) for a specific purpose, although in many cases price is often a deciding factor in this. The fillers are used in either starch mangle or back-filling operations."

Miscellaneous Uses

Talcs, clays, bentonite, diatomite and other mineral powders are used as dusting agents for molds of many types and for the manufacture of sheet goods. Mineral powders are used as lubricants in greases and in a dry condition for metal parts, tires and rubber goods. Talcs, graphite, and clay are most commonly used. Antisticking agents are related.

In some compositions, the fillers of lighter bulk density are useful as fluffing or bulking agents. Dentifrices, inks, leather dressing, match heads, artificial leather, window shades, cosmetics, and various other products, utilize mineral fillers either as part of the compositions or at some stage in their manufacture.

Various mineral products are used as fillers in heat and sound insulating compositions, and in other light-weight products. These are considered elsewhere in this book. In mortars, cements, stuccos and concrete, finely divided mineral powders may be added as fillers, admixture, treating agents or as puzzolanic ingredients. Substantial tonnages of bentonite, silica, diatomite, talc, lime and other materials are used for these purposes.

Whiting, clay, talc, diatomite and other fillers are employed in the manufacture of linoleum and other types of floor coverings, either in the base composition or in the lacquer surfacings. The incorporation of fillers in the surface coating improves the gloss thereof and increases the resistance to wear and abrasion as well as to the action of the commonly used detergents.

Asbestos, as the only important fibrous mineral material, is employed as a filler and as a reinforcing material for many compositions—asbestos-cement products, mill boards, roofings, roof coatings, sealing compounds, putties, plasters, molded articles, welding rods, paints, greases, floor tile, plastics and other compositions. Powdered rocks and minerals also are used in many of these types of products.

METHODS OF TESTING AND SPECIFICATIONS

Testing procedures for each of the properties listed hereinbefore as important for mineral fillers cannot be given here. Some of these are required for research purposes only while others do not differ materially from methods of general use.

For technical control in manufacture, for the writing of specifications and for the usual inspection tests by purchasers, the following are of most general interest: color, grit content, residues on standard testing sieves, apparent densities, moisture content, chemical analysis, presence of impurities, pH, particle size, specific surface and liquid absorptive capacity.

TABLE 2—*Some ASTM Testing Methods and Specifications*

Abbreviated Title	Designation	Volume Number in 1946 Standards	Pages
Tests			
Tentative Qual. Exam., Mineral Filler and Coating of Paper.....	D686-46T	III B	1229-1233
Tentative Particle Size Distrib., Subsieve Size Particulate Substances.....	E20-33T	III B	1292-1296
Sieve Analysis Mineral Filler.....	D546-41	II	545-546
Alkalinity or Acidity of Pigments.....	D-278-31	II	922
Analysis: Al Silicate Pigment.....	D718-45	II	928-931
Ba Sulphate Pigments.....	D715-45	II	932-935
Diatomaceous Silica Pigment.....	D-719-45	II	936-937
Magnesium Silicate Pigment.....	D717-45	II	938-940
Mica Pigment.....	D716-45	II	941-943
Specifications			
Title	Designation	Volume Number in 1946 Standards	Pages
Ba Sulphate.....	D602-42	II	875
Al Silicate (China clay).....	D603-42	II	876
Diatomaceous Silica.....	D604-42	II	877
Magnesium Silicate.....	D605-42	II	878
Mica.....	D607-42	II	879
Pumice (tentative).....	D867-467	II	1540

Many special tests within particular industries are employed, and an increasing number of these have become rather generally accepted. Committee D-8 on Bituminous Waterproofing and Roofing Materials, Committee D-1 on Paint, Varnish, Lacquer and Related Products, Committee D-6 on Paper and Paper Products, Committee D-11 on Rubber and Rubber-like Materials, all of the American Society for Testing Materials, have adopted tentative and standard methods and specifications. Publications by TAPPI (Technical Association of Pulp and Paper Industry) give further detail of particular interest to manufacturers and dealers. Abraham¹³ has included most test methods for asphalt fillers. For paint extender pigments, see Gardner³⁴ and Mattiello.³⁶ Some ASTM testing methods and specifications are listed in Table 2.

For some properties, which are still difficult to define precisely and in which there are differences in methods, it is customary in many filler-consuming industries to prepare specifications by reference to a standard reference sample, thus: "The *X* property shall be equal to that of a reference sample mutually agreed upon by the purchaser and the seller." While empirical and not without objection, this method has much merit and is of considerable aid in maintaining uniformity and conformity within satisfactory limits.

Some references to particle size and surface area tests are given in the bibliography because of their importance for filler specifications. Now that more satisfactory methods have been developed, some of them comparatively simple, the more general use of particle-size distribution and surface areas is being demanded for many filler uses.

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CHAPTER 28

MINERAL PIGMENTS

BY CHARLES L. HARNESS*

MINERAL pigments give color, opacity, or body to paint, stucco, plaster, mortar, cement, linoleum, rubber, and similar materials. They must be finely divided, substantially insoluble, and generally inert for such uses.

Inorganic pigments may be grouped somewhat arbitrarily as follows:

A. Natural mineral pigments dug from the earth.

1. Those consisting mostly of iron oxides, such as hematite and limonite.
2. Those containing large amounts of clay or noncoloring matter, such as ocher, sienna, umber, and colored shales.
3. Those whose color is not due to iron oxide, such as Vandyke brown (including sap brown, an alkali extract of Vandyke brown), graphite, and terre verte.

B. Synthetic pigments.

1. Those containing iron oxide as the essential coloring matter, such as "pure" reds, yellows, and blacks, and Venetian reds.
2. Those not containing iron oxide, such as lithopone, zinc white, titanium white, ultramarine, Prussian blue, and the like.

Only groups A and B-1 are discussed here. All the pigments in those two categories, except Vandyke brown, sap brown, and some of the carbonaceous slates, contain, as their essential color constituents, one or more compounds of iron; namely, an oxide—limonite ($2\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ to $\text{Fe}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$), hematite (Fe_2O_3), or magnetite ($\text{Fe}_2\text{O}_3 \cdot \text{FeO}$).

Man's first permanent coloring materials were earth pigments—the ochers, iron oxides, and various iron-stained clays. The caves occupied by prehistoric man and the arts of the ancient Chaldean, Egyptian, and Cretan civilizations bear mute witness to this and also testify to the beauty and permanence of earth colors. As the Roman era developed, earth pigments were pushed from their pre-eminent position by white lead and red lead and in the Middle Ages by zinc oxide. Today, of course, the number of acceptable pigments is very large and on a value basis the group of natural and synthetic earth pigments stands

* American Cyanamid Co., Stamford, Connecticut.

forth with \$8,000,000 per year; it is surpassed by titanium, lead, and zinc pigments. Of this sum, as of 1946, the share of the natural earth pigments was 36 pct, the remainder representing the value of sales of the synthetic iron oxide colors. Tonnagewise, however, sales of natural earth pigments in 1946 were 62 pct and of the synthetic, 38 pct, of the total.

NATURAL EARTH PIGMENTS

Although the synthetic iron oxide pigments are more important than the natural colors, any discussion of the two does well to start with the

Raw: Yellow, yellow-brown Burnt: Red, red-brown, salmon		Dark brown to black
OCHERS	SIENNAS	UMBERS
Fe ₂ O ₃ 17 to 60 pct	Fe ₂ O ₃ 25 to 75 pct	Fe ₂ O ₃ 37 to 60 pct
SiO ₂ 35 to 50 pct		MnO ₂ 11 to 23 pct
	MnO ₂ , small percentage	
Al ₂ O ₃ 10 to 40 pct	SiO ₂ 10 to 35 pct	SiO ₂ 16 to 35 pct
	Al ₂ O ₃ 10 to 20 pct	Al ₂ O ₃ 3 to 13 pct
	Loss on ignition, 10 to 12 pct	Loss on ignition, 15 to 20 pct

FIG 1—APPROXIMATE COMPOSITION OF EARTH PIGMENTS.

naturals, because these are most important historically and because they provide standards for comparing the synthetics that followed.

Yellow and Yellow-brown—Yellow ocher (mineral yellow, Roman ocher or earth, Chinese yellow, and others) comprises a clay (about 70 pct) stained with limonite (typically about 19 pct, Fe₂O₃ basis), the remaining 11 pct being mostly water of hydration.

As shown in the accompanying chart (Fig 1), ochers may grade into siennas with increasing Fe₂O₃ content, and siennas may grade into umbers with increasing manganese dioxide content. However, there are no hard and fast dividing lines, and one well-known earth pigment mined near Cartersville, Georgia, containing 54 pct Fe₂O₃, has been

* called a sienna about as often as it has been called ocher. A true sienna is much more transparent than an ocher. At one time French ochers led the field in sales of natural yellow pigments but even before the late war these imported yellows were being displaced on the American market by natural yellows containing considerably more iron oxide (about 54 pct as against 20 pct—a factor making for increased chroma and dilutability—as well as by the pure synthetic yellow iron oxides.

Red and Red-brown—The hue of natural red pigments is derived from hematite. Outstanding examples are Persian red and Spanish red. Persian red contains 65 to 72 pct Fe_2O_3 . It is imported from Ormuz Island, in the Persian Gulf. Most of it is ground in England and the United States for reshipment. The mass tone is rich crimson but when “let down” with zinc oxide, the tint is bluish. Spanish red is a fairly pure hematite mined near Jaen in the province of Andalusia and shipped from Malaga on the Mediterranean coast. During World War II, a number of domestic replacements for Spanish red came on the market but, as far as is known, no replacement for Persian red was offered. Exports of both pigments appeared in 1947 to be limited by shortages of processing and packing equipment rather than by external demand.

Browns—Most important in the brown class are the metallic browns (incompletely calcined siderite or limonite), siennas, umbers, and Vandyke brown. Domestic raw siennas are a strong brown; Italian siennas are yellow-brown. In either case, on calcining, the yellow limonite and ferrous oxide content are converted to red ferric oxide and black carbonaceous matter is burned out, with consequent brightening. The overall result is a beautiful red with a brownish cast. Raw umbers are dark brown-blacks and when burned are a dark brown with a bluish undertone. In the old Italian sienna-burning industry, the lumps of raw sienna were spread out on hot brick. This process gave a gradation of siennas, with the reddest at the bottom, and careful selection was necessary to ensure color uniformity. In the United States, the muffle furnace was standard for a time but now most domestic siennas and umbers are calcined in rotary kilns with a bare flame. Siennas and umbers are suitable for stains, since much of the iron is present as iron silicate, which is fairly transparent in drying oils. It might be supposed that burnt siennas and umbers would be more costly than the uncalcined variety, but the reverse is commonly true; a certain amount of control during calcining permits a uniform result even when working with varied raw material, whereas the range of blends possible with raw siennas and umbers is quite limited, these pigments generally occurring in small pockets and at infrequent intervals. Vandyke brown, a weak pigment, is made from peaty matter and its color is due to organic matter, of which it contains about 70 to 92 pct, rather than to its 1 pct of iron oxide content.

Blacks and Other Pigments—The only earth pigments approaching a true black are magnetite, graphite, and perhaps a few carbonaceous slates. Of these only magnetite (94 to 95 pct Fe_2O_3) is used commercially, mostly in metal primers. Green and blue earth pigments (such as terre verte and lapis lazuli) are not on the market today and have only a minor historical significance.

PROPERTIES

Color—The yellows, browns, and reds of the earth pigments apparently have been esthetically pleasing ever since the dawn of modern man. The colored sketches on Cro-Magnon cave walls, on Egyptian friezes, on Greek pottery, and the extensive use of these pigments in Renaissance art, attest freely to an appreciation of these warm-hued, permanent colors. The dominant wave lengths range from about 582 millimicrons for pure yellow to 605 for pure red. Pure yellow has the greatest light reflectance (is the most brilliant), and dark raw umber has the least.

Particle Size—Earth pigments consist of minute particles ranging in size from finely divided colloidal clay and hydrated ferric oxide to hard rocks that after grinding are just finer than 325-mesh. Ordinarily, the smaller the particle size, the greater the reflectance, brightness, and hiding power. However, there seems to be an optimum particle size for each pigment, and particles that are too small tend to scatter blue and green light and thus reduce reflectance in the lower wave lengths. Particles in raw umber smaller than 1.2 microns fail to reflect the characteristic olive undertone that is the chief attraction of that pigment, and raw siennas lose part of their greenish cast if ground below 2 microns. On the other hand, particles above the desired range will cause a rough paint film. The maximum percentage weight coarser than 325-mesh allowed by the American Society for Testing Materials for the red and brown iron oxide pigments is 2.0 pct and for ocher only 1.5 pct. Love and Ayers⁵ suggest particle-size ranges for all the important earth pigments.

MODE OF OCCURRENCE AND DISTRIBUTION OF DEPOSITS

Since the coloring power of the natural yellow, red, and brown mineral pigments is due principally to the content and condition of iron oxide, the occurrence of mineral pigments in many instances is closely allied to that of the iron ores. Pigment materials and iron ores often are mined in the same localities, and iron ores are used at times for mineral pigments of the red and brown varieties. The iron oxides are almost universally distributed.

Replacement or precipitation deposits are the principal sources of limonite and ocherous minerals. They have been deposited in cavities

by ground waters charged with iron salts removed from the weathering of impure limestone, sandstones, and shales, especially when pyrite was an accessory mineral. The most important deposits are found usually in the fractured and faulted zones of rocks of all ages, including the Cambrian quartzites of Georgia, the Paleozoic limestones and quartzites of Pennsylvania, and the unconsolidated Tertiary clays, sands, manganese ores, and lignites of Vermont.

In the state of Virginia, deposits of residual limonite occur in two belts, one extending along the west slope of the Blue Ridge from Warren to Roanoke County and the other along the east side of the New River-Cripple Creek district, Pulaski County, and near the Wythe-Carroll County boundary. The latter deposits are associated with Cambrian quartzites. Within the past few years the deposits in Pulaski County have been developed, producing ochers of high iron content somewhat similar in analysis and properties to the Georgia ochers.⁵

The chief production of earth pigments in the United States in recent years has come from Pennsylvania, Virginia, Illinois, Minnesota, Georgia, California, and New York.

France (near Apt, in the Department of Vaucluse) supplies ochers; raw and burnt siennas are exported from northern Italy. On the Island of Cyprus, Turkey umbers are mined, and excellent hematites are shipped from Spain and the Persian Gulf, as already mentioned. Numerous other localities furnish earth pigments for local consumption and occasionally for the world market.

COMMERCIAL CONTROL, PRODUCTION, AND CONSUMPTION

During World War II, the United States was virtually independent of imported earth pigments, furnishing all requirements from local mines, supplemented by synthetics. Fairly successful replacements were found for every type of foreign pigment except Persian red.

Import duties on ochers, siennas, umbers, and iron oxide and iron hydroxide pigments are provided for in paragraph 73 of the Tariff Act of 1930, as amended. The rates of duty on these items as of 1948 were as shown in Table 1.

In 1942 the Bureau of Mines initiated a canvass of sales of iron oxide pigments processed from domestic raw materials. Figures on quantity and value for 1946 and 1947 are shown in Table 2.

Under Section 337, Title III of the Tariff Act of 1930, foreign-made pigments may not be imported into the United States royalty-free if they are made by a process protected by a United States patent. An interesting case is cited wherein this law was invoked.¹¹

PROSPECTING, EXPLORATION, AND MINING

A beautiful red, yellow, or brown color is the principal indication of a mineral pigment in the field. Unfortunately, most rocks and clays so

TABLE 1—*Duties on Imports of Earth Pigments, United States, 1948*

Pigment	Duty Cents per Lb
Ochers:	
Crude or not ground	$\frac{1}{8}$
Washed or ground	$\frac{1}{8}$
Siennas:	
Crude or not ground	$\frac{1}{8}$
Washed or ground	$\frac{3}{8}$
Umbers:	
Crude or not ground	$\frac{1}{16}$
Washed or ground	$\frac{3}{16}$
Iron oxide and iron hydroxide not specially provided for:	
	Pct ad Val.
Synthetic	15
Other	20

TABLE 2—*Natural Mineral Pigments and Manufactured Iron Oxide Pigments Sold by Processors in the United States, 1946-1947, by Kinds^a*

Pigment	1946		1947	
	Short Tons	Value	Short Tons	Value
Mineral blacks.	6,369	\$118,171	<i>b</i>	<i>b</i>
Precipitated magnetic blacks.	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
Natural brown oxides (metallic browns). .	5,823	276,379	5,861	\$308,440
Vandyke brown (finished pigment).	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
Sap brown.				
Pure browns (96 pct or more iron oxides). .	1,018	206,806	1,016	219,686
Natural red oxides.	22,436	972,405	20,524	946,997
Pure red oxides (98 pct or more Fe ₂ O ₃). .	17,050	3,117,706	17,331	3,481,083
Venetian reds.	9,727	721,354	7,127	579,603
Pyrite cinder.	964	52,471	1,682	110,863
Other red iron oxides.	17,345	1,683,166	18,817	2,214,358
Natural yellow oxides (high Fe ₂ O ₃).	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
Pure yellows (85 pct or more Fe ₂ O ₃).	9,527 ^c	1,293,379 ^c	10,496	1,635,365
Ochers (low Fe ₂ O ₃).	10,774 ^c	250,168 ^c	9,130	213,133
Siennas:				
Burnt.	1,197	168,978	940	141,943
Not burnt.	2,401	303,483	1,441	201,493
Umbers:				
Burnt.	3,727	325,856	3,051	322,668
Not burnt.	916	68,615	671	61,443
Other.	5,823 ^c	445,213 ^c	17,280	730,066
	115,097	10,004,150	115,367	11,167,161

^a Data from U. S. Bureau of Mines.^b Included under Other.^c Revised.

colored are already diluted with aluminum silicates and other impurities and their pigment strength is inadequate except for local consumption, perhaps for coloring mortar. Very few colored rocks when powdered and mixed with 10 or 20 times their weight of zinc oxide or white lead will produce more than a perceptible tint, because of the low concentration of iron oxide. Therefore, a prospector's equipment should include a small porcelain mortar and pestle for fine-grinding small samples of colored rocks with at least 10 times their weight of zinc oxide. These should be compared side by side with samples of various commercial pigments diluted in the same proportion in both the wet and dry condition.

In Pennsylvania, ocher is mined by both opencut methods and shafts, and in Georgia by opencut methods. In most deposits the pockety character of the ore and the uncertain market for the product do not justify elaborate equipment. Typical mining operations are described by Wilson.¹³

The soft, claylike pigments are treated by comparatively simple washing processes, followed by dehydration and pulverization. Log washers and blungers are used for dispersion; trough, cone, and bowl classifiers separate the sand from the fine suspension. A portion of the water is removed in settling tanks and the remainder is extracted by filter presses and rotary driers. Pulverizers of the hammer type reduce the pigment to powder for packing and shipment and a final air separation may be interposed for the better grades.

SYNTHETIC PIGMENTS CONTAINING IRON OXIDE

As far as is known, the first commercial synthetic iron oxide pigment made in the United States was copperas calcined by alternative processes; i.e., either in a reverberatory furnace (the American process) or in a muffle furnace (the English process). The product was washed, ground, and bagged. The English process gave a better pigment for years, until the even temperatures of the muffle could be duplicated in the rotary kiln.

The next advance in the synthetic field was the precipitation of black and yellow iron oxides by adding lime to a copperas solution but this was soon superseded by a less expensive yellow, produced by immersing scrap iron in the solution and blowing in air. The yellow so obtained analyzes over 97.5 pct ferric hydrate and 0.15 pct soluble salts. Reds were obtainable by calcining the yellows.

The synthetics are characterized by uniform fine particle size, friable structure—making for easy grinding, high covering power, color permanence, good protection of paint film against ultraviolet light, and resistance to water, acids, and alkalis.

The more important United States patents on synthetic iron oxide pigments are listed in reference 10.

TESTS AND SPECIFICATIONS

The problem of identifying desirable and undesirable characteristics in a given pigment and matching it colorwise with a previously determined standard has received a great deal of attention in the past half century. A number of standardized tests have been developed for analysis and appraisal of pigments, with the object of eliminating the human equation. The incomplete success of this mass of criteria is found in the almost universal requirement in modern pigment specifications: "The mass color and character of tint formed by mixture with a white pigment shall be the same as, and the strength not less than, that of a *reference sample* [*italics supplied*] mutually agreed upon by the purchaser and seller." This generally brings the appraisal back to a personal, visual basis.

Among the chief characteristics of pigments tested are mass color (appearance of the pigment when "rubbed out" in oil), tinting strength (appearance when diluted in zinc oxide oil paste), particle size, oil absorption, opacity, and chemical composition.

Mass Color—Accurate color analyses that indicate the percentage of reflection or luminosity for each wave length can be made by spectrophotometers, colorimeters, photometers, and other color analyzers, and the curves can be plotted.² The mass color is commonly determined roughly by making a comparison of the sample pigment with some approved color chart or system. American Society for Testing Materials Specification D387-36, Test for Tinting Strength and Mass Color of Color Pigments,¹ describes an accepted procedure for testing mass color and tinting strength.

Tinting Strength—Tinting strength, or the power of coloring likewise, is commonly determined by comparison with a standard pigment. The two pastes are compared side by side after a thorough mixing of each with the same amount of standard white zinc oxide oil paste (see ASTM Specification cited above). If quantitative results are needed, the amounts of pigments may be varied until the tinting strength is the same; then the ratio of the amounts of pigments provides an index of tinting strength of the sample.

Particle Size—The maximum allowable percentage of grit determined by washing with water ranges in various specifications from 0.5 pct (for synthetic iron colors) to 2.0 pct (for natural pigments) on a 325-mesh (44-micron) sieve. Grit can be detected by the teeth, which are very sensitive to hard, sandy particles. The particle sizes that are important for tinting strength are finer than the finest sieve openings, and special tests are necessary for this determination. ASTM test E20-33T, Particle Size Distribution of Subsieve Size Particulate Substances,¹ for example, uses microscopic examination with statistical in-

terpretations. Other methods stress water elutriation, sedimentation, air flotation, and opacity determinations.

Oil Absorption—As a general rule, the amount of drying oil required to give a plastic suspension with a pigment should be kept to a minimum. Hence knowledge of the oil absorption is important. An accepted method of determining this is given in ASTM specification D281-31, Oil Absorption of Pigments.¹ The linseed oil required to produce pastes of equal consistency ranges as follows for a number of commercial pigments: French ochers, 30 to 37 pct; American ochers, 35 to 53 pct; raw sienna, 25 to 70 pct; raw umbers, 44 to 53 pct; yellow oxides, 29 to 49 pct; red oxides, 14 to 28 pct.

Opacity and Hiding Power—The property that enables a paint or pigment to obliterate the background or to reflect the incident light before it reaches the background varies with the total pigment surface in a given area of paint and with the difference in refractive indexes of the oil and pigment. As a rule, the hiding power varies inversely with the particle size down to the point at which the particle is so small that it scatters light rather than reflects it. Various hiding-power tests are described by Gardner.²

Chemical Composition—The usual chemical analysis of mineral pigments, giving the percentage weights of silica, alumina, iron oxide, lime, magnesia, alkalies, and ignition loss, indicates the total quantity of iron oxide, the accompanying coloring ingredients if any, and the type of base, such as clay or gypsum, but does not give definite information about the original color, the mineral constituents of the diluting base material, or the important physical characteristics, such as color, fineness of grain, workability, and degree of iron oxide dispersion. The chemical analysis can be used in standardization tests for specific pigments to maintain certain minimum requirements for the chief coloring ingredients and it will also reveal objectionable materials. An accurate and complete analysis, however, is expensive and difficult, whereas practical physical tests are easy and require little time.

The very general nature of the requirements found in the Government and private specifications indicates the minor importance of chemical analyses in comparison with physical tests. The United States Government and the American Society for Testing Materials require a minimum Fe_2O_3 content of 17.0 pct for ocher, a maximum of 5.0 pct CaO , and absence of organic coloring matter and lead chromate.

MARKETING, USES, AND PRICES

The miner of a mineral-earth pigment must decide whether to sell it crude to a pigment processor or to process it and sell the finished material to a paint manufacturer, or to make it into a paint. Owing to the many refinements introduced into pigment processing in recent

years, a large capital outlay is generally required to invade this field, and most miners find it more convenient to sell to an established processor, who also has the advantage of access to a number of varihued pigments from other sources and can keep blended pigments of uniform color and texture on the market year after year. Prices for most raw pigments are little more than the cost of mining; prices for the relatively rare strikes of good sienna and umber may be double or more the cost of mining.

Uses

The main use of the pigments containing iron oxide is in paints, wood and paper stains, oilcloth, linoleum, window shades, mortar colors, roofing granules, plaster, rubber, plastics, imitation leather, mastic floor tile and other pigmentable materials. A time-honored use of iron oxide (natural or synthetic hematite) is jewelers' polishing rouge. Ground hematite, sometimes but not necessarily of pigment grade, is used in compounding certain stock and poultry feeds and as a weighting agent in oil-well drilling muds. In the pigment field, the iron oxides are used (as a coating over red lead) as rust inhibitors, in metal priming, in ship-bottom paints, and for railroad structures and rolling stock. Siennas, umbers, and Vandyke and sap brown are used as wood and paper stains, the latter material being added to paper pulp in the beater.

Prices

In tune with the inflation that followed World War II, prices for earth pigments were generally higher in 1947 than at any time since the late twenties. In the Nov. 10, 1947 issue of the *Oil, Paint and Drug Reporter*, the following prices were noted, in less carlots, cents per pound, barrels, New York City, or works: Precipitated magnetic blacks, 10; metallic brown, $2\frac{3}{4}$ to 3; synthetic (pure) browns, 12 to $12\frac{1}{2}$; burnt siennas, American type, $6\frac{3}{4}$ to $10\frac{3}{4}$; Italian-type burnt siennas, $10\frac{3}{4}$ to 14; American-type raw siennas, $5\frac{3}{4}$ to $10\frac{3}{4}$; raw siennas, Italian type, $11\frac{3}{4}$ to $12\frac{3}{4}$; Turkey-type burnt umbers, $5\frac{1}{2}$; Vandyke brown, 10 to 11; sap brown crystals, 12; synthetic (pure) red iron oxides, $10\frac{1}{2}$ to $10\frac{3}{4}$; Venetian reds, $3\frac{1}{10}$ to $4\frac{4}{10}$, depending on iron oxide content; natural (metallic) red oxide, $2\frac{1}{2}$ to $2\frac{3}{4}$; natural yellow oxides, high iron, $4\frac{1}{4}$; and synthetic (pure) iron oxide yellows, $8\frac{1}{2}$. Generally speaking, prices were highest in the boom of the late twenties—for example, natural yellow oxide was $6\frac{1}{4}$ in 1926, synthetic (pure) yellow 12 in 1929, and Italian burnt siennas $12\frac{1}{2}$ in 1930—but there are exceptions, some maxima being observable in the early depression years and some prices today exceeding even those of the post World War I boom period. In the latter category are American raw siennas (4¢ in 1925); American burnt siennas (4¢ at previous maximum of 1932); and metallic browns ($2\frac{1}{2}$ in 1925).

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CHAPTER 29

MINOR INDUSTRIAL MINERALS

BY PAUL M. TYLER*

MINOR industrial minerals included in this chapter are: the alum minerals, bromine, calcium chloride, epsomite and other natural magnesium salts, iodine, meerschaum, quartz, industrial crystals other than quartz (Iceland spar, tourmaline, fluorite, selenite, mica), and nonfuel gases (air, helium, carbon dioxide).

ALUM MINERALS

The alums comprise a series of double sulphates (or selenates) isomorphous with potash alum, which, according to a ruling of the Pennsylvania courts, is the only product commercially described simply as "alum." Common alum occurs in nature as kalinite ($\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$). The mineral mendozite ($\text{Na}_2\text{SO}_4)_3 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$) is soda alum; tschermigite ($(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$) is ammonium alum; and there are about a dozen other native alums and related double sulphates. Alunite (alumstone or alum rock) has the formula $\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 4\text{Al}(\text{OH})_3$ and alunogen, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. Saline residues, found wherever natural water is evaporated, may contain sulphate of alumina, which for most uses is the essential ingredient of alum. Mineral wells and springs that emerge from beds of pyritiferous shale are typically astringent and at times form local deposits of alum, generally as incrustations. Acid waters acting upon aluminous rocks may form sulphates of alumina.

The alums of commerce, as well as aluminum sulphate (concentrated alum), are produced principally by treating bauxite with acid, but they have been made also on a substantial scale from clay, cryolite, pyritic slates, schists, lignites, alunite, and leucite. Alum shale—chiefly clay, pyrite, and (usually) carbonaceous matter—was extensively used in England as a source of alum for more than two centuries. In France, pyritic lignites mixed with sand and clay were burned in heaps to red ash, the leach liquors from which, after treatment with ammonia, yielded alum and copperas. Processes have been developed for making alum or aluminum sulphate from such diverse materials as feldspar, aluminous phosphate minerals, greensand, and mixtures of mica and

* Mineral Technologist, Economist, Kensington, Maryland.

potash salts or of clay and alkali sulphates—most commonly by baking the material with sulphuric acid at low red heat.

Kalinite occurs in an irregular network of veins associated with sulphur in rhyolite in Esmeralda County, Nevada. At a recovery plant operated there between 1920 and 1923, the ore was crushed to $\frac{3}{4}$ -in., ground to pass about 80-mesh, and leached (countercurrent); the resulting alum solution was then filtered and crystallized. Occasionally, kalinite-bearing rocks are baked with acid to increase the yield, and if the natural liquor does not contain enough potash to form potassium alum, potassium sulphate may be added.

Alunite received a great deal of attention during World War I as a source of potash and during World War II as a source of alumina. In Europe, it was used at one time rather extensively for making potash alum. Although insoluble in its natural state, the mineral is readily decomposed into K_2SO_4 and Al_2O_3 by heating to above about $750^\circ C$. Deposits are found in several western states—Utah, Colorado, Nevada, Arizona, and California—and have been mined at Marysville, Utah, and at Sulphur, Nevada.

Production and Consumption of Alum

Alum was being produced commercially in the United States as early as 1815, the domestic industry receiving its first impetus from the cutting off of imports during the war of 1812. Alum-making from bauxite was begun in 1877 and in 1880 the Census reported that six establishments produced some 19,600 tons of alums valued at \$808,165. A half century later, the domestic output of alums was not much greater and during the 1930s it was generally still under 25,000 tons annually. The output of aluminum sulphate, on the other hand, then ranged from 300,000 to 400,000 tons a year. All of these figures increased sharply during the recent war and in 1945 the industry produced 8460 tons of ammonia alum, 4844 tons of potash alum, 557,271 tons of commercial aluminum sulphate, 29,731 tons of iron-free sulphate and 28,842 tons of sodium aluminum sulphate. The aggregate value of these products was around \$16,000,000. Imports normally are small, seldom exceeding about 1000 tons a year prewar, whereas exports have generally ranged during the past decade from 35,000 to 50,000 tons annually, mostly aluminum sulphate to Canada.

In 1939, the manufacture of alums and aluminum salts in the United States consumed 178,000 long tons of bauxite and minor amounts of other materials. In 1945, when the output was substantially larger, the consumption of bauxite was only 134,766 tons, as other raw materials were used, including 13,000 tons of aluminum trihydrate, 91,000 tons of clay, 13,523 tons of secondary aluminum, and a quantity of alunite and bichromate residue.

Markets and Prices of Alum Minerals

Aluminum sulphate generally is marketed in two grades, both containing about 45 pct combined water and approximately 37 pct SO_3 : (1) iron-free (under 0.1 pct Fe_2O_3); and (2) commercial. The theoretical composition calls for 18 molecules of water but this product tends to be sticky, so the commercial product may be evaporated to a content of about $14\text{H}_2\text{O}$ and, for at least one important use, down to $7\text{H}_2\text{O}$. A very small quantity of anhydrous sulphate is sold. Aluminum sulphate is mostly crushed and bagged or barreled. The usual container is a 200-lb jute bag; paper-lined bags have been used to some extent and experiments are being made with 100-lb paper bags. The alums are available in various technical grades (lump or powdered) and also as C.P. crystals and as U.S.P. crystals, granules and powder. Sodium-aluminum sulphate, however, is marketed commercially only in anhydrous condition, generally ground. So-called "porous alum" is ordinary aluminum sulphate to which a very small amount of soda ash was added just before solidification, thereby liberating enough carbon dioxide to fluff it up and thus make it more quickly soluble; as the ground product is being more generally used than lump, porous alum is of less importance than formerly.

A leading use of potash alum is for treating furs, though it has some medicinal and special uses. Ammonium alum is used, largely in lump form, for making statuettes and other cast-stone or stucco products and it may be employed instead of potash alum for sundry purposes. Sodium-aluminum sulphate (not soda alum) is almost exclusively sold to baking-powder manufacturers, who buy it ground.

As mordants in dyeing, for making lake pigments, for the dressing of skins ("tawing") to produce white leather, and in the clarification of water, sewage, and turbid liquids generally, aluminum sulphate has displaced the true alums almost completely. Water purification and paper account for much of the consumption of this material, and surprisingly large quantities are used in fire-fighting compounds. There are many miscellaneous uses—such as dyeing textiles, tanning leather, and decolorizing or deodorizing mineral oils—but these account for scarcely 5 pct of the total consumption.

Prices on alums and aluminum sulphate do not change frequently; quotations have remained about the same week after week for years. In the middle 1930s, the New York price of iron-free aluminum sulphate was \$2 per 100 lb and the commercial grade was listed at \$1.35. For both ammonia and potash alums, prices during the interwar period began around \$3, the latter generally (though by no means always) being slightly the higher. Sodium-aluminum sulphate, or so-called "soda alum," normally is in about the same price range or only a

trifle higher; it contains more sulphur trioxide but its other ingredients, of course, are cheaper. Average values f.o.b. works of specified products, as calculated from Bureau of Mines production statistics, are as follows for 1945 (1939 figures in parentheses): Potassium alum, \$68 (\$58); ammonium alum, \$77 (\$53); aluminum sulphate, commercial, \$22 (\$20); iron-free sulphate, \$36 (\$25); and sodium aluminum sulphate, \$65 (\$51) per short ton.

BROMINE

Bromine (Br_2), a dark, reddish brown, highly corrosive liquid, does not occur uncombined in nature but is widely distributed in the form of bromides, usually accompanying common salt and magnesium chlorides. It is present in sea water to the extent of 67 parts per million and higher concentrations occur in certain well brines; those in Michigan carry up to 2.5 pct. Commercial sources in the United States include brine wells and bitterns in California, Michigan, Ohio, Pennsylvania, and West Virginia; and (principally) sea-water plants first in North Carolina and subsequently in Texas. Bromine is also one of the products obtained from Searles Lake, California. The earliest production in the United States was from saline springs along the Kanawha River, West Virginia, but for many years the world's bromine came mainly as a by-product of potash operations in Germany. At one time there was some production from the great salt marsh near Montpelier, in southern France, and following the return of the Alsatian potash fields after the first World War, France once more became a producer under an agreement with the German cartel similar to that covering potash. Palestine became an important factor in the European situation during the interwar period, the Dead Sea product being used extensively in England, which formerly had imported bromine from the Continent. Italy, Japan, Russia, and Tunis have all produced commercial quantities of bromine and virtually all salt-producing countries are potential suppliers.

Production of Bromine

Although bromine was produced in the United States as early as 1846, there was no real demand for it until 1860, and the industry virtually began in 1865 with the recovery of less than 2000 lb from the Stassfurt deposits. A year or two later, saltmakers in the Pomeroy district, Ohio, began to recover bromine more or less regularly and domestic output grew to more than a million pounds at the beginning of the twentieth century, only to drop to a quarter of that figure in 1910 as a result of competition from Germany, which already had produced more than two million pounds in a single year. Wartime needs of the United States and its allies boosted domestic output to a peak of 1,727,156 lb in 1918, chiefly as sodium bromide. Following a postwar reces-

sion, production in this country began rapidly to expand as a result of the increasing use of bromine in connection with the manufacture of antiknock gasoline. By 1929, it had risen to 6,414,620 lb and in 1939 to 37,882,000 lb. It jumped to 59,266,000 lb in 1940 and the new wartime peak was 94,086,000 lb, valued at \$19,713,000, in 1944.

Less than 3 pct of that produced in the United States is sold as elemental bromine; over 90 pct is marketed in the form of ethylene dibromide and the remainder is comprised in the several bromides, of which potassium bromide is most important. Ethyl-Dow Chemical Co., the largest producer, now recovers its bromine from raw sea water only at Freeport, Texas. Dow Chemical Co., Midland, Michigan, second largest producer, and four other companies produce it from Michigan well brines. The American Potash and Chemical Corporation, Trona, California, recovers bromine from Searles Lake; Westvaco Chlorine Products Corporation recovers the element from sea-water bitters at Newark and Chula Vista, California, and from well brines in West Virginia.

In 1939, the United States was producing more than 80 pct of the world output. At the same time, Germany produced 10 pct, Palestine and France each about 5 pct, and Italy about 1 pct. Notwithstanding the dominant position of domestic production, imports of bromine, chiefly as ethylene bromide, averaged over a million pounds a year immediately before Hitler's troops invaded Poland.

Bromine Technology

The initial installation using the blowing out process for recovery of bromine from raw sea water was established on a peninsula a little above the mouth of Cape Fear River, near Wilmington, North Carolina. By discharging the effluent on the opposite side of the peninsula, dilution of the incoming water was avoided. After fish and debris have been removed in rotary screens, the raw water is acidified with H_2SO_4 , treated with chlorine, and then pumped to the top of the blowing-out towers, where the liberated bromine is blown out by compressed air. The sea water remains in the plant undergoing treatment for scarcely one minute. The bromine is caught in large absorption towers using soda-ash solution. The resulting mixture of sodium bromide and bromate is then treated with acid and the free liquid bromine is collected in columns, from which it goes to the reactors and combines with gaseous ethylene to form ethylene dibromide.

Elsewhere, bromine is produced from natural or artificial brines, usually from the concentrated bitters remaining after the sodium chloride has been recovered. Recovery is accomplished commercially by one of three distinct methods: (1) a batch process using sulphuric acid and an oxidizing agent (such as sodium chlorate or manganese

dioxide); (2) a continuous process involving treatment with chlorine gas; and (3) another continuous process in which an electric current instead of chlorine is employed to liberate the bromine.

Markets and Prices of Bromine

The recovery of bromine from the Stassfurt deposits, begun in 1865, soon reduced the price from \$10 to \$4.50 a pound and within a few years to \$1.30. By 1880, it was down to 7¢ a pound (0.70 mark per kilogram) in Germany and 25¢ a pound in the United States. The wholesale price of bulk bromine in New York ranged from 25¢ to 35¢ a pound in 1913, soared to \$6.50 in 1916, and finally reached a wartime plateau at around 55¢. After leveling off again at 45¢ to 47¢ in 1926, it receded in March 1931 to 36¢ to 38¢. Continuing the downward trend, bottled elemental bromine in cases, carlots, works, was quoted at 25¢ to 30¢ in 1942 and 21¢ in 1944–1945. Potassium and sodium bromides, U.S.P., granular, 500-lb barrels, works, were quoted at 25¢ a pound in 1945. The average unit value of the bromine contents of domestic output, f.o.b. plant or shipping point, has generally been well below quoted prices. It rose from 13¢ in 1910 to a peak of \$1.31 in 1916, dropped to 15¢ in 1922, rose to 34¢ in 1926, receded to 21¢ in 1931, and then gradually drifted below 20¢. In 1945, the average value of bromine contents of all products was a trifle over 18½¢ but the average for elemental bromine alone was about 17½¢. For sodium and potassium bromides, the 1945 averages were around 20¢ a pound (gross weight); for ammonium bromide, 22½¢, and for ethylene dibromide, about 15¢.

For almost two decades, bromine has been used predominantly as ethylene dibromide, for making tetraethyl-lead antiknock compounds; recently nearly 90 pct of the total domestic output of bromine has gone into this use, which is largely an integrated operation conducted by the Ethyl-Dow Corporation, in conjunction with the Ethyl Gasoline Corporation and the Dow Chemical Co. Outside of this enterprise, liquid bromine is consumed principally in fumigants, dyes, medicinals, and photographic chemicals, and in organic syntheses. It is packed for shipment in cases containing nine 6½-lb bottles. For use as analytical reagent, a small though important use, it is available in 1-lb bottles. Bromides other than ethylene dibromide used for making ethyl fluid are sold to large chemical-manufacturing organizations in bulk containers weighing 100 to 500 lb net. These manufacturing organizations either consume these bromides by compounding with other products to make pharmaceuticals or repackage them in small containers for marketing through retail drug channels.

Previous to about 1923, bromine was used principally in the form of sodium potassium, or ammonium bromide, in photography and for medicinal purposes. The substantial revival in demand after the Armis-

tice came from the motion-picture industry and there is a steady consumption for medicinal purposes, notably the treatment of nervous diseases. It is used for making fluorescein, eosin. Hoffman's blue, brom indigos, and other organic coloring matters for use in dyeing. During the first World War, some hand grenades and gas bombs were loaded with bromine or with organic bromine compounds. Brombenzyl cyanide, a tear gas for use in the trenches, was invented in 1917. "Mining salt," a mixture of sodium bromate and bromide, was formerly used in some quantity for the extraction of gold from its ores, but this use seems to have virtually disappeared. However, acetylene tetrabromide has possibilities in the mining field in heavy solutions for separating ores; its use has been reported in South America for recovering diamonds, and experimental plants have been operated in this country on various ores (Nagelvoort process). It is used in the automobile industry for oil and gasoline gauges.

Lower prices for bromine and the knowledge that inexhaustible supplies are obtainable from the ocean have stimulated research looking toward a larger use of bromine for organic syntheses and in metallurgy and some progress has already been made toward its use for sterilizing water. During the recent war, bromine solution was used to some extent in Germany for disinfecting wounds, replacing tincture of iodine.

CALCIUM CHLORIDE

Calcium chloride (CaCl_2) occurs as an original constituent of natural brine and is produced commercially in connection with the extraction of salt or of salt and bromine. The calcium chloride thus recovered ordinarily contains a substantial admixture of magnesium chloride and small amounts of other salts, and for certain uses this naturally mixed calcium-magnesium chloride need not be further purified or separated. The principal commercial source of calcium chloride is as a by-product of the Solvay process for the manufacture of sodium carbonate, the chlorine content in such case being derived from brine or rock salt but the calcium coming from limestone. In Germany, in addition to being a by-product of the Solvay process, it is recovered by the potash companies from carnallite ($\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), which often carries as much as 3 pct CaCl_2 . Calcium chloride is actually listed as a distinct mineral, hydrophilite or chlorocalcite, occurring as a crystalline or mealy incrustation in the neighborhood of active volcanoes and, rarely, elsewhere, as an impure, slimy exudation from sandstone, or mixed with clay. The hydrous calcium chloride ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) is known only in artificial crystals (hexagonal). Commoner are mixtures with magnesium chloride and other alkaline chlorides, notably tachydrite ($\text{CaCl}_2 \cdot 2\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$). Fluorspar (CaF_2) contains chlorine but only in minute quantities.

Anhydrous calcium chloride is a white, deliquescent substance that fuses at a red heat and, on cooling, solidifies to a translucent mass of cubic crystals of specific gravity 2.2. Its characteristic property is its avidity for water. Even crystals of the hydrated chloride ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$) deliquesce rapidly, dissolving in only one fourth their weight of water at room temperature. A fused product may be purchased in C.P., U.S.P., and technical grades, but the principal commercial grades are: (1) flake (77 to 80 pct); solid (73 to 75 pct); and liquid (40 to 45 pct).

Currently at least half and formerly more than 90 pct of the potential output of by-product calcium chloride must be thrown away because of lack of market. The bulk of the marketed production comes from Solvay soda-ash operations although variable and generally increasing quantities are derived from underground brines. Domestic production almost trebled in value and more than trebled in quantity between 1923 and 1929, reaching a peak in the latter year of 277,010 short tons having an average value of \$21.47 per ton (converted to 73 to 79 pct basis). In 1929, the output of calcium (calcium-magnesium) chloride from natural brines, as reported by the Bureau of Mines, was 114,240 tons valued at \$18.36 per ton. After remaining around 100,000 tons a year throughout the 1930s, it rose rapidly to a peak of 224,527 tons valued at \$1,733,000 in 1942 and subsequently held at roughly double prewar figures.

Uses and Prices of Calcium Chloride

The principal use of calcium chloride is for stabilizing rural roads. It is generally bladed into the surface during the spring when the roadbed is moist and pliant. State and local government highway boards, therefore, are the leading purchasers. Ice control on streets and sidewalks and use by railroad and bus companies rank second in importance, circulating brines at refrigerating plants (formerly the only large commercial outlet) now coming third. Next in order comes the treatment of coal and coke and sundry other dustproofing or freezeproofing uses, and considerable quantities are employed in curing concrete (high early strength). Among miscellaneous uses may be mentioned fire buckets and preserving the freshness of oak leaves and natural foliage. As an antifreeze, it finds employment in cooling condensers in the oil and gas fields but is not recommended for automobile radiators; although not corrosive of itself, it causes electrolytic attack where two or more metals are in contact. In addition to being the standard laboratory desiccant, it is used as a dehydrant in several industries, as a dehumidifier in air conditioning, and as a rust preventive for munitions parts or other metal articles wrapped in moisture-proof coverings such as pliofilm. Of popular interest are recent experimental uses for dispersing fog and for preserving tobacco seed.

Although highway construction and upkeep account for so large a proportion of the consumption of calcium chloride, sales are not distributed geographically in proportion to population or road mileage. Michigan uses much larger quantities than might be expected and there is an abnormally high consumption also in parts of Ohio and Indiana and in the vicinity of Chicago. The use of calcium chloride, however, has been spreading to other states and even to localities remote from producing centers, where freight rates add greatly to the cost. Production from the ammonia-soda process is concentrated in New York, Ohio, and Michigan, and the output from natural brines, although there are as many as a dozen producers, all comes from three states—California, Michigan, and West Virginia. It follows that transportation is a real factor in delivered prices. Thus flake chloride in carload quantities (77 to 80 pct; minimum $22\frac{1}{2}$ tons) has generally been quoted at delivered prices ranging, according to zone, from \$18 to \$35 a ton. Solid calcium chloride is generally \$2 a ton cheaper than flake and liquid is still cheaper in most localities on the basis of equivalent chloride content and the usual price of \$7.50 a ton for 40 pct solution tank cars f.o.b. works. In terms of 75 pct $(\text{Ca,Mg})\text{Cl}_2$ content, the average unit value of sales reported by the Bureau of Mines remained almost unchanged around \$8 a ton during the period 1941 to 1945.

Exports generally are in excess of imports but both are normally rather small, averaging less than 10,000 tons a year.

EPSOMITE AND OTHER NATURAL MAGNESIUM SALTS

Epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) is deposited from spring waters, as at Epsom, Surrey, England, and has been mined near Oroville, Okanogan County, Washington and elsewhere, although never to any large extent. Kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$), which is found chiefly at Stassfurt, Germany, and Hallstatt and Kalusz, Galicia, and which can be readily separated from associated saline minerals because of its relatively slow solubility, is used as raw material for epsom salts, which are made also from magnesite and dolomite.

According to Census reports, domestic production of epsom salts in 1935 was 38,489 tons valued at \$1,116,533, and imports were 1530 tons. Kieserite formerly was imported in substantial quantities from Germany, but, notwithstanding the fact that it is specifically free of duty under the Tariff Act of 1930, few shipments have been reported in recent years. Imports of epsom salts, likewise, have diminished greatly and now are confined largely to Norfolk, Virginia, where they are distributed to tobacco growers as fertilizer.

The Bureau of Mines reports production of MgSO_4 from natural brines only, excluding the larger production from neutralizing caustic-

calcined magnesia with sulphuric acid, as well as additional quantities that have been made from olivine and serpentine. On a 100 pct basis, the sales of "natural" magnesium sulphate were 27,142 tons valued at \$1,377,311 in 1945.

Magnesium sulphate, fertilizer grade, 65 pct, bags, carlots, delivered at eastern consuming points, was quoted at \$59.50 a ton in 1945; industrial grade, 80 pct, at 5 to 5 $\frac{3}{4}$ ¢ a pound. Although best known for its medicinal properties, MgSO_4 is employed extensively as a rayon coagulant, in tanning, in pharmaceuticals and stock feeds, and as a fertilizer.

IODINE

Iodine (I_2) is a gray or purple-black, crystalline solid, semimetallic in appearance and diffusing a chlorinelike odor. The vapor is one of the heaviest known gases, 8.8 times as heavy as air. Its characteristic color gave the element its name, which is derived from the Greek word for "violet." Solid iodine (sp gr 4.9 +) is the heaviest nonmetallic element. In chemical affinity, it resembles other members of the halogen group although it is markedly less energetic, and because of its high atomic weight (126.9), much larger quantities are required for a given reaction. Though almost insoluble in pure water, iodine is very soluble in solutions of potassium iodide, owing to formation of a compound, KI_3 .

In minute quantities, iodine is widely distributed throughout the animal, vegetable, and mineral kingdoms. It is always present in sea water but not in sufficiently large amounts to offer promise for its direct commercial recovery. A few varieties of seaweeds, however, are able selectively to absorb the element within their cell structure, especially at certain seasons of the year, and a good deal of iodine has been recovered from the ash or "kelp" obtained by carefully burning such weeds as were harvested along the storm-swept coasts of Ireland, Scotland, France, Norway, Russia, and Japan. The bulk of the world's iodine, however, has come as a by-product from the working of the natural nitrate deposits in Chile, where the iodate minerals dietzeite and lautarite have been identified in the caliche. In Java, salt wells yielding 0.1 gram or more of iodine per liter have been worked for iodine since before 1900 and, beginning about 1925, Italy has developed a small industry based upon brine wells at Salsomaggiore. Production from oil-well brines began in California and Louisiana in 1928 and by 1932 had reached commercial proportions. Similar sources have been developed in Russia, Poland, and Mexico. Iodine in small quantities has been found in various sedimentary deposits, especially coal, and a potentially commercial concentration of iodine (0.1 to 0.3 pct) in Cottrell-precipitator flue dust at an iron blast furnace in Czechoslovakia was traced back in large part to the coke.

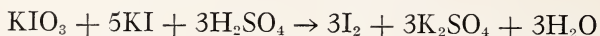
Production of Iodine

The output of iodine is geared to world demand, which has increased rather slowly. During the interwar period, it was about 1000 tons, roughly three times the quantity sold in 1887. Immediately before the first World War, it was only 500 tons and a maximum output of 1500 tons was reported in 1915. Chile has furnished almost three fourths of the world supply and could easily expand its production several fold.

Except for an insignificant quantity recovered in California as a result of wartime experiments with seaweed, the United States, while consuming one third of the world consumption, produced no iodine until 1928. By 1933, three plants were extracting iodine from certain waste oil-well waters in California and their sales totaled 401,525 lb. The latest year for which domestic production figures can be shown is 1937, when 299,286 lb valued at \$242,422 was produced. Output in recent years has been considerably higher but there have been only two producers and no figures can be reported. The bulk of the domestic consumption is still supplied by Chile. Imports rose to a peak of 2,744,930 lb in 1943 and averaged 1,226,228 lb annually during the 5 year period from 1941 through 1945, but any consumption figures calculated simply from international trade statistics are likely to be in error on account of the huge stocks of Chilean iodine that have been accumulated at various times in the United States and in other countries.

Iodine Technology

In the Guggenheim-process plants in Chile, the iodine dissolves in the nitrate leach liquors in concentrations of 5 to 10 grams per liter. By addition of sodium bisulphite (made from Na_2CO_3 and SO_2), the iodate is reduced to iodide; then, by addition of 20 pct more of the original solution, the following reaction can take place:



The iodine sludge is filtered, pressed into a cheesecake, and retorted to a crude product of blue-black lustrous crystals, 99.4 pct pure.

Various other precipitants can be employed, including direct gassing with SO_2 . In Java, the iodine is recovered in the form of insoluble cuprous iodide. In the French seaweed industry, 25 tons of weed shrink to 5 tons when dried and yield 1 ton of ash, from which not more than 25 to 30 lb, more often scarcely half this quantity, of idoine is obtained. Potash salts constitute a joint product at most plants and common salt also may be recovered. Algin, a sticky, nitrogenous substance used for sizing or waterproofing textiles, is sometimes recovered from the raw weed.

For treating California oil-well brines, which contain only 30 to 70 parts of iodine per million, there are two successful processes. In one,

the iodine is liberated in the acidulated brines by an oxidant, usually Cl_2 , and absorbed in activated carbon; in the other, or silver process, it is precipitated quantitatively by adding AgNO_3 . These waters contain considerably more Br_2 than I_2 , but recovery of Br_2 has not been considered worth while.

Markets and Prices of Iodine

Chilean crude iodine is packed in wooden kegs holding about 60 kg, which are sewed in rawhide to protect them in shipping and also to hold together the staves when, as not infrequently happens, the steel hoops corrode and drop off after years in storage. The Iodine Association specifies a minimum purity of 99 pct and not more than 0.1 pct acidity (calculated as H_2SO_4), but even the crude product ordinarily runs 99.5 pct. Iodine sublimes readily (bp 184°C) and is obtained in high purity by this treatment. Crude iodine has relatively few purchasers, principally manufacturers of its salts, many of which are official in the United States Pharmacopeia. A rough estimate shows that eventually it is marketed about as follows: potassium iodide, 70 pct; sodium iodide, 5 pct; resublimed iodine, 15 pct; all other compounds, 10 pct.

Lack of iodine in the human system is said to be one cause of goiter, so iodine salts are employed for internal antiseptics; also for treatment of high blood pressure, arteriosclerosis, and a variety of other ills of man and beast. In certain localities, all table salt has to be "iodized," and some municipal authorities require iodine to be dissolved in the drinking-water supply for the community. Iodine and its compounds are valuable laboratory reagents and have important uses in photography. Uses are found also in dye manufacture, tanning, and other industries, but iodine is far too expensive in comparison with chlorine or even bromine to encourage its wide employment industrially. At present, the most promising field for expansion of consumption is the addition of potassium iodide to stock feed. This costs only 5¢ per ton of feed and is said to be of great benefit to animals. By extending the medicinal uses of iodine to cover animals as well as humans, a fivefold expansion in iodine consumption is envisioned.

Selling prices of crude were fixed for many years by the Chilean Producers' Association at 12d an ounce (about \$3.89 a pound) f.a.s. vessel, with a 2.5 pct discount on 500-lb orders. Delivered at New York, it was worth around \$4 a pound. It has been estimated that the nitrate companies could have sold iodine profitably at 25¢ a pound but as long as the only competition was from seaweed iodine, costing \$2 to \$3 a pound, the Chilean group (Corporation de Ventas) withdrew from the international cartel and sought to reestablish themselves in the important American market. Prices were reduced progressively and efforts were made to expand demand through laboratory research and a general educational program.

By May 1, 1936, the New York price of crude iodine was cut to 90¢, resublimed iodine to \$1.65 to \$1.50 a pound, and leading salts were correspondingly reduced. These prices were subject to a 5 pct discount on quantity purchases. On Oct. 10, 1936, the price was once more revised downward to 81¢ a pound, with no quantity discounts. Beginning in 1942, the Office of Price Administration placed a ceiling price of \$1.28 $\frac{1}{4}$ per pound on crude iodine (150-lb kegs). Resublimed iodine in 5-lb bottles was selling at \$2 to \$2.10 a pound in 1945.

MEERSCHAUM

Meerschaum ($H_4Mg_2Si_3O_{10}$) is a soft (hardness, 2 to 2.5), fine-grained, earthy, white, gray, or yellow material. The name "meerschaum" (German for "sea foam") suggests light weight; the specific gravity is given as 1 to 2 but when pure and dry it will float on water. Owing to its resemblance to the porous, bonelike structure of the cuttlefish or sepia, the mineral is also known as "sepiolite." When wet, the material is soft, even somewhat plastic, but it becomes hard and tough after drying again, the toughness being more apparent in varieties that have a fibrous or leathery texture.

There are a few scattered deposits of meerschaum in the United States that have yielded a small production but the world's supply of the material is obtained principally from Asia Minor. Meerschaum deposits near Eskişehir, Turkey, have been worked for centuries, possibly as early as 2000 years ago, and during the past 100 years their product has enjoyed a large European market, being much carved in Vienna. World production, virtually all from Turkey, is reported to have exceeded 10,000 boxes, weighing 30 to 35 kg each, in 1869. According to some reports, the exports in prewar years often amounted to 7000 boxes annually. Since about 1924, however, the output has declined, the annual average being scarcely 500 boxes. American deposits may have yielded a total of 1000 tons, chiefly from a deposit near Sapillo Creek, New Mexico. Meerschaum has also been obtained from the islands of Euboea and Samos, Greece; near Hrubšitz, Moravia, Czechoslovakia; in Bosnia; in Morocco; and near Vallecás, Madrid, and Toledo, Spain; but mines in those countries, never extensive, were closed many years ago. A related mineral, aphrodite, is found near Langbanshyttan, in Vermland, Sweden.

Mining, Preparation, and Uses of Meerschaum

Meerschaum usually occurs as an alteration product of magnesite, serpentine, or possibly impure opal high in magnesium. The Turkish deposits occur in a valley filled with drift material from the surrounding mountains. The drift has been partly cemented by lime and the meerschaum occurs as scattered nodules, the size ranging from that of an egg to that of a football. These nodules are brought to the surface and worked

on the spot, those from the dry pits being worth more than those from the wet. They are sorted according to complex grading, depending upon size and quality, before being packed in the boxes. The mining is primitive, pits are dug by pick and shovel to a depth of 60 to 100 ft with only enough timbering to allow the workmen to climb up and down. Nodules are recovered by a system of untimbered drifts and crosscuts, the ore being hoisted to the surface in baskets by a windlass. Floods and cave-ins are common occurrences. Government aid, largely in the form of loans to the owners of the pits, has been extended recently to the Turkish mining industry but, according to latest reports, the Eti-Bank had not taken over the working of the pits.

Virtually the only use of meerschaum is in smokers' articles, and meerschaum from any source but Turkey seems to have proved unsuitable. The making of meerschaum pipes was begun more than 200 years ago (1723) in Budapest. Somewhat later, in 1767, the industry was undertaken in Ruhla, in the Thuringian Forest, Germany, and subsequently the manufacture of pipe bowls and cigar holders from genuine and artificial meerschaum has been centered principally in that town. The making of meerschaum pipes consists in roughly cutting the irregular masses to shape, carving by hand or turning down on lathes, and smoothing with glass paper and Dutch rushes. They are then boiled in wax, stearin, or spermaceti, and polished with chalk or bone ash. The color of meerschaum deepens with smoking, owing to absorption of a mixture of nicotine and the finishing wax. The color continues to deepen as long as any wax remains but when the desired color is reached it may be set by removing the remaining wax and boiling in linseed oil to fill the pores and harden the mineral. Details of the color-setting process are trade secrets. Before setting, the color may be destroyed if the pipe is subjected to excessive external heat (such as washing in very hot water or drying too quickly). Artificial meerschaum pipes may be made from meerschaum chips and dust compressed into blocks. Imitation meerschaum is prepared by treating hardened plaster of paris with wax and coloring with gamboge or other pigments. Pipes made from this material are susceptible to color change, as are the genuine meerschaum pipes.

At Vallecas, Spain, meerschaum is said to be used as a light building material, and in Turkey and Algeria it has been employed instead of soap. Meerschaum has also been used as an ingredient in porcelain.

Markets and Prices of Meerschaum

Aside from the sporadic domestic production, much of which was unsalable, all meerschaum used in the United States has been imported. Imports amounted to 16,646 lb valued at \$22,649 in 1924 but dropped to 788 lb valued at \$2,536 in 1933.

Market quotations relate to cases of standard size and (like those for oranges) vary according to the size of the individual pieces in the container. The number of pieces per case may range from only 35 to several thousand. For material large enough to be made into pipe bowls, the size is not so important as the quality, and for each of these sizes there are as many as seven grades, ranging in price from \$155 to \$335 a case. Small pieces sell as low as \$30 a case. It is difficult to translate these quotations to a weight basis but the statistics for imports into the United States show that the average foreign market prices per pound have ranged from a minimum of \$1.60 to well over \$3 per pound in recent years.

Under the Tariff Act of 1930 (paragraph 1552) a duty of 20 pct ad valorem is levied on crude meerschaum.

QUARTZ*

Silica (SiO_2) or quartz occurs in crystalline (quartz, tridymite, and cristobalite), cryptocrystalline (chalcedony), or amorphous (opal, diatomite) forms. As generally used, the term "quartz" includes virtually all sands, sandstones, and quartzite, as well as rock or vein quartz. Next to the feldspar group, quartz is the most abundant mineral in the earth's crust and it appears in a greater number of varieties and modes of occurrence. Silica, free or in combination with other elements, constitutes 59.08 pct of the lithosphere and quartz alone represents fully 12 pct of all rocks.²⁵ Being hard (No. 7 on the Mohs scale), moderately tough, resistant to acids, refractory, and often transparent, quartz has physical and chemical properties that, particularly in view of its abundance in nature, have led to a multiplicity of uses in industry.

Domestic production statistics for quartz might properly include those for sand and gravel, quartzite, and other highly siliceous items that are discussed separately in this volume in accordance with their commercial classifications. Relatively pure quartz is a by-product at several feldspar mines and the total marketed production of crude, crushed and ground quartz in the United States from pegmatites, veins, or quartzite rose in 1943 to 99,445 short tons, valued at \$345,558, the largest tonnage since 1917, when 142,673 tons was reported. Much of this quartz was used in newly built wartime plants for making ferrosilicon in the Pacific Coast states. In 1945, the total was down to 57,764 tons, of which 24,392 tons worth \$72,392, or \$2.96 a ton, was sold crude; 28,718 tons, worth \$93,631, or \$3.26 a ton, was sold crushed; and 4,654 tons, worth \$70,780, or \$15.25 a ton, was sold in ground condition. To avoid duplication, the ground material so reported is only that ground by the original producers of the crude quartz or by grinders who purchase from

* See also chapters on Abrasives, Dimension Stone, Granules, Quartz Crystals, and Special Sands.

farmers or small miners not reporting to the Bureau of Mines. Both crude and crushed quartz are bought by various mills that grind silica flour for ceramic uses, paints, and so forth. They are used also as metallurgical flux, for filling acid towers, and for sundry miscellaneous uses.

Quartz rock and sand may be priced at less than 50¢ a ton and in many localities a good grade of lump quartz can be bought for \$1 or \$2 a ton, or about the same price as glass sand. Pulverized quartz competes in a slightly lower price range with tripoli and other "soft silicas," varying all the way from \$6 to \$35 a ton. In recent years, dry-ground silica sand of suitable color has been used in substantial quantities for the manufacture of asbestos-cement products. The high prices of silica flour, of course, are due principally to the cost of grinding. However, at the top of the price list of quartz products is rock crystal, the value of which depends upon its internal structure. Radio-grade crystals were purchased by the Government during the recent war under a sliding scale ranging from \$1.56 to \$36.95 a pound, according to quality. Crystals employed in making fused-quartz products are somewhat cheaper, being quoted in 1947 at \$100 to \$150 a ton, and optical or jewelry stock is intermediate in price.

Quartz-crystal oscillators and resonators assure accurate frequency control for electrical circuits and were needed by the millions to equip the allied armies. Piezoelectric-grade quartz, the raw material for these devices, is therefore a necessary component of radio transmitting and receiving sets, detection devices, long-distance telephone transmission lines, and various precision instruments. Virtually throughout the second World War, this material alternated with condenser-grade mica (also used in communications) as the No. 1 strategic mineral. Because of their strategic importance, quartz crystals are discussed in a separate chapter of this volume.

INDUSTRIAL CRYSTALS OTHER THAN QUARTZ

Large and more or less perfect crystals of most minerals are in fair demand as specimens for display in public museums and private mineralogical collections. A surprising number of different minerals find employment in costume jewelry. Marcasite, for example, seems to be used rather extensively for this purpose. The radio industry, now the chief user of quartz crystals, formerly required rather large quantities of pyrite and/or galena as essential components of the early crystal sets. Minerals having certain refractive indexes or other special characteristics are employed in minor amounts in the optical industry, which, of course, demands transparent pieces that are structurally sound, free from mechanical strains, and uniform in chemical composition.

New types of glass, plastics, and, to a minor extent, artificially grown crystals have replaced natural crystals for special optical uses in part but

not entirely. On the other hand, synthetic stones have largely replaced natural stones in jewel bearings for watches, clocks, and metering instruments. A few industrial sapphires are still produced by placer mining but the quantity is almost negligible in comparison with the total demand. The manufacture of synthetic sapphires, theretofore conducted only in Europe, was initiated in the United States successfully on a large scale during the recent war. Diamonds probably are the only crystals now being used industrially in large and growing quantities for which there is no reasonably satisfactory substitute.

Iceland Spar

By far the most important optical mineral other than quartz is the variety of calcite known as Iceland spar. This form of calcium carbonate is characterized by its purity, transparency, and perfection of crystalline structure. The strong double refraction of Iceland spar is utilized in the nicol prism, a device that transforms ordinary light into plane-polarized light. Before it can pass through calcite, an incident ray of light is split into two rays, designated respectively as "ordinary" and "extraordinary," both of which are unidirectional in their vibrations.

Nicol prisms are an essential part of every polarizing microscope and are used also in saccharimeters, dichroscopes, photometers, colorimeters, spectrometers, polariscopes, and any other instrument that makes use of polarized light. The ordinary petrographic microscope, which has two nicol prisms, provides an accurate means of identifying most minerals by observing the behavior of plane-polarized light in traversing thin sections of the unknown material. Owing to its unidirectional vibration, polarized light is similarly invaluable in the other instruments mentioned and in the determination of crystal structure by modern X-ray analysis.

In making a nicol prism, a cleavage rhombohedron of Iceland spar, about three times as long as it is wide, is cut diagonally along the plane connecting the obtuse dihedral angles of two opposite elongated faces and the end surfaces are ground down until they are perpendicular to the plane of this cut. The two halves are then cemented together with Canada balsam. After polishing, the cemented prism is mounted in cork that has been blackened so as to absorb light that is reflected from the sides.

During the second World War, Iceland spar was seriously considered as material for gunsights. The concentric rings that are apparent when one looks through a slice of calcite can be used for aiming at a target and are preferable in certain respects to the older type of metal-ring sight. However, because of excessive difficulty of obtaining dependable supplies of natural raw material, the use of Iceland spar for this

purpose was quickly discontinued in favor of synthetic materials or different instrument designs.

Until recently, Iceland spar was considered as having no substitute in polarizing microscopes and other scientific instruments, but Polaroid, the same plastic material that replaced spar in gunsights, has been used in petrographic microscopes. Whether synthetic materials are universally competitive or merely supplementary to Iceland spar is a question that cannot yet be answered positively.

Only a small percentage of the Iceland spar recovered from most deposits is of optical grade. As impure, cloudy, or otherwise imperfect calcite crystals are no more valuable than ordinary limestone, the proportion of rejected material is large. The finest museum specimens are usually of optical grade and the numerous smaller fragments sold to museums, colleges, schools, or private collectors as additions to collections or for demonstration of optical properties are usually also of high quality. Typical Iceland spar fluoresces a strong and beautiful red color and so makes superb specimens for mineralogical cabinets. Small fragments of high purity are marketable in small quantities. They are virtually pure CaCO_3 and are used for standardizing in analytical chemical laboratories and plant-control work.

Most of the commercial deposits of Iceland spar have been in rather small pockets, containing redeposited masses or crystal aggregates along with residual clay. Such deposits are characteristically associated with igneous rocks. Minor deposits, usually of inferior quality, occur as vein material in limestones and related rocks.

The famous deposit from which the material derived its name is situated in Iceland, not far from Eskifjörður. It was discovered early in the seventeenth century but received scant attention for several decades and was not actually developed as a commercial source of spar until 1850. In 1877, the Government took over control of all operations. During the first World War, mining was discontinued and the quarry was flooded "to protect the crystals from weathering." Although reopened later, the deposit has since been worked only spasmodically and the quality of the product has been unsatisfactory.

During the interwar period, the principal source of world supplies shifted to South Africa, notably the Kenhardt district, northwest Cape Province. The deposits there are numerous but small and scattered erratically over a large area. The spar occurs as irregular masses of various sizes embedded in cavities filled with soft, sandy clay. Mining began in this region in 1915 and 20 years later the grand total South African output to that date was estimated as not exceeding 2000 lb, most of which was shipped to Germany.

Spain, Canada, and several Latin American countries (recently including Mexico) have contributed occasional shipments of spar of good

quality, although never in large amounts. Little is known definitely regarding the resources in Russia but they are believed to be ample for her own needs.

Domestic deposits have been reported in several western states. Some time before Pearl Harbor, the late Dr. E. M. Stanton opened up what seemed like a large deposit near Taos, New Mexico, and made substantial shipments that included many remarkably large pieces of excellent quality. Subsequently, he lost control of the deposit and mining operations were abandoned. In 1942-1943, Calcite Operators, Inc. conducted fairly large-scale mining and exploration in northeasterly San Diego County, California, where the spar occurs in veins and pockets in the Palm Springs (Tertiary) formation. There was some wartime activity in Colorado and Nevada and some promising developments in Montana especially in the vicinity of Greycliff, Sweet Grass County, and Big Timber, Park County.

The mining of Iceland spar presents certain interesting and unusual features. The material is soft (No. 3 on the Mohs scale) and easily shattered. Rough treatment is likely to initiate incipient fractures or strains that ruin the optical properties, even though no visible damage occurs. The use of explosives should be avoided as far as possible. The clay matrix doubtless affords some protection to the crystal masses, but, even in breaking the rock envelope, experience has shown that the most careful blasting is likely to ruin much good material. As an alternative to blasting, a California correspondent once suggested a novel method of breaking the rock. Holes are drilled as usual, but, instead of being loaded with explosives, they are partially filled with quicklime tamped around a slender iron bar or thick wire. The wire is carefully withdrawn and a wet cotton string is inserted into the small hole. The collar of the drill hole is sealed with tightly rammed clay. As the lime slakes, the steady pressure breaks the rock slowly, with a minimum of shock.

Production and consumption statistics for Iceland spar are not available. It is common knowledge that wide fluctuations occur from year to year and that on several occasions what appeared to be a serious shortage was changed quickly to a glut when a bushel or so of crystals was offered for sale. Normal needs of the United States have been estimated at 200 or 300 lb a year but the average probably is much less.

Prices are determined by negotiation between buyer and seller and vary widely. During the interwar period, the range was between \$7 and \$35 a pound and the latter figure was characteristic of wartime transactions. Good museum specimens usually fetch \$1 to \$3 a pound, although substantial premiums may be paid for extra fine crystals or large rhombs. Standardizing spar is worth a little less than collectors' specimens, and may vary from \$1 to \$2 a pound, unground.

Tourmaline, Fluorite, Selenite, and Mica

Tourmaline is a mineral of much interest to physicists because of its optical and electrical properties. It is a possible substitute for piezoelectric quartz but, unfortunately, is seldom found in large enough crystals free from cracks. It also has pyroelectric properties. Like Iceland spar, this mineral has double refraction. A crystal of tourmaline transforms a ray of light into an "ordinary" ray vibrating perpendicular to the principal axis and an "extraordinary" ray vibrating parallel to this axis. As the ordinary ray is strongly absorbed, plates cut parallel to the principal axis transmit essentially only the extraordinary ray, and so are used as a polarizing medium. When placed at right angles, such plates cut off all light. Two plates, properly mounted, form the instrument known as the "tourmaline tongs," which is used for testing spectacle lenses and for simple laboratory demonstrations of polarized light.

Fluorite has a low index of refraction, disperses light faintly, and normally displays no double refraction. Accordingly, selected crystals of this mineral are used in lenses and lens systems to correct spherical and chromatic errors. In a telescope, for example, a fluorite element eliminates undesirable color effects. Another use of optical-grade fluorite is in spectrographic and other apparatus where transparency of nonvisible rays—both ultraviolet and infrared—is essential.

Although quite rare, optical fluorite may be found as occasional small crystals at almost any commercial fluorspar operation. Water-clear specimens are preferred but faintly tinted crystals can often be used for optical purposes. Prices vary widely, depending upon supply and demand at the moment as well as upon the size of flawless crystals or cleavage fragments.

Selenite, the water-clear variety of gypsum, composes the sensitive plate of a polarizing microscope that is used to reveal the slightest double refraction in mineral thin sections.

Mica is another mineral accessory of the petrographic microscope, being used in the form of a thin plate to determine the optical sign of a mineral section.

NONFUEL GASES

Natural gas, in ordinary parlance, is a mixture of hydrocarbons, chiefly methane, but the gas from certain fields contains from a trace to 2 pct or more of helium, together with traces of argon and neon. Nitrogen and carbon dioxide are even commoner components, a few gases carrying more than 80 pct N_2 . Hydrogen sulphide occasionally is present in objectionable amounts, "sour" gases requiring processing to remove it. A few gas wells produce highly concentrated carbon dioxide, and gaseous or vaporous emanations almost universally accompany

volcanic activity. Of the volcanic gases, water vapor naturally is the most abundant. It has been harnessed to steam turbines for commercial power production, notably in Italy, where boric acid is jointly recovered from the vapor springs. Dry fumaroles emit sublimates of metallic salts, chiefly chlorides, mixed with atmospheric air. Acid fumaroles pour out water vapor charged with hydrochloric acid and minor amounts of sulphur dioxide; in other fumaroles, the water vapor is heavily charged with hydrogen sulphide or free sulphur, the latter being sometimes recovered commercially. Sulphur dioxide and carbon dioxide, says Clarke,³⁰ never occur together, although hydrogen sulphide and carbon dioxide often come from the same fumarole, the proportion of carbon dioxide gaining as volcanic activity diminishes. The gases that issue from an active crater contain superheated steam, hydrogen, carbon monoxide, methane, vaporized metallic chlorides, and a variety of substances of minor importance, such as oxygen, nitrogen, argon, sulphur, and fluorine compounds. As temperatures drop, the nature of the exhalations changes until finally only steam, with possibly a little carbon dioxide, remains. Aside from fuel gases, steam, boron compounds, and sulphur (certain deposits of which are characteristically of fumarole or solfataric origin), the commercial natural gases that are from the earth are helium and carbon dioxide.

Air

The air we breathe, however, can be described as a mixture of gaseous minerals, and "mining air" yields compressed air for power transmission and other purposes, and liquid air. Liquid air has been used as an explosive, but principally as a source of oxygen. Oxygen, 99.5 pct pure, is isolated in enormous quantities for use mostly in welding, though substantial quantities are used in treating pneumonia and other respiratory diseases.

Production of oxygen in the United States, principally by three large companies, increased from 3 billion cubic feet in 1929 to 4½ billion in 1939 and a top total of 18.7 billion in 1944. The great wartime expansion was due mainly to the wide use of oxygen cutting instead of mechanical sawing, shearing, and scarfing in steelworks and fabricating plants. Oxygen-enriched air—when it becomes available at low enough cost—has great promise in process metallurgy, oil refining, and processes for making synthetic liquid fuels, and possibly also in the manufacture of city gas. Low-purity oxygen at ordinary pressures probably can be produced in large private plants for local use at between 10¢ and 20¢ per 1000 cu ft, well below \$5 a ton. Some estimates are even lower. Although high-purity liquid oxygen, as now distributed, cost in 1947 scarcely more than one fourth as much as it did in 1921, even consumers of large quantities pay in the neighborhood

of \$3 per 1000 cu ft (expressed at standard temperature and pressure) and users of small quantities may pay as high as \$20. Formerly, the largest container was a cylinder weighing 125 lb, which held only 18 lb of compressed gas (220 cu ft), but shipments can be made now in tank cars and trucks holding as much as 62,000 lb.

Nitrogen from the air has broken the Chilean nitrate monopoly, thereby making explosives manufacturers in leading countries independent of overseas deliveries of raw material and giving the farmer an unlimited supply of cheap fertilizer. Argon and neon likewise are won from the air, the former being used to fill ordinary incandescent

TABLE 1—Basic Data for Liquefaction of Air^a

Constituent	Volume, Pct	Boiling Point, Deg K	Critical Temperature, Deg K
Air.....	100	79	132.3
Nitrogen.....	78.03	77.19	126.0
Oxygen.....	20.99	90.04	154.2
Argon.....	0.94	87.16	156.
Hydrogen.....	0.01 ^b	20.56	33.1
Neon.....	0.0015	26.7	53.
Helium.....	0.0005	4.02	5.2
Krypton.....	0.00011	120.1	210.
Xenon.....	0.000009	165.9	258.
CO ₂ ^b	0.03–0.07	194.00 ^c	304.1
H ₂ O ^b	0.01–0.02	373.0	647.

^a *Chemical Engineering* (March 1947) 127.

^b Variable constituent.

^c Solid CO₂ sublimes.

electric lamps and the latter for the now familiar illuminated tubes for advertising signs as well as for sodium vapor lamps, glow lamps, and sundry electrical “trouble-shooting” devices. Krypton and xenon, the remaining “minerals” of the air, are far too scarce to command commercial significance; they can now be purchased but a quantity sufficient even to inflate a football would cost hundreds of dollars.

Virtually all processes for the separation of constituent gases from the air are based upon liquefaction and fractionation. Liquefaction is accomplished always by combining compression with refrigeration. Basic data have been tabulated by the editors of *Chemical Engineering* as shown in Table 1.

Helium

Helium is colorless, absolutely inert; odorless, tasteless, nonpoisonous, nonflammable. It furnishes a safe atmosphere for welding magnesium, stainless steel, and aluminum. Mixed with oxygen, it provides a breathing atmosphere that mitigates caisson disease (“the bends”) in

deep-sea diving. Much larger quantities of this mixture are used in treating asthma. Extensive test work is underway using this gas as a tracer and wider use is anticipated in metallurgical work, for medical purposes, and in scientific studies, but the predominant use is as lifting medium for balloons and airships, and the United States Government is the only large producer and consumer. Helium has a lift of 66 lb per 1000 cu ft, compared with 71 lb for inflammable hydrogen, the lightest known gas. During the second World War, it was used chiefly to inflate aircraft for coast patrol, although additional large quantities were consumed by the Weather Bureau for meteorological balloons and by the Army for inflating barrage balloons. Army balloons, however, were mostly filled with hydrogen that could be generated in the field, whereas helium had to come from the United States.

As recently as 1917, helium sold at the rate of \$2,500 for cubic foot and was available in very small quantities. The pioneer plant at Fort Worth* was closed in 1929 and the peacetime needs of the country were subsequently supplied by a plant at Amarillo, Texas, constructed and operated by the Bureau of Mines. This plant made a 90 pct recovery and a 98 pct pure product and held the gas rights in 50,000 acres of land in the Cliffside field. Before Pearl Harbor, it was capable of producing 24,000,000 cu ft of gas annually. Since this capacity was never completely utilized for long periods, the total actual production by the Government prior to Dec. 31, 1941, including 49,000,000 ft produced by the original Fort Worth plant, was only 180,000,000 ft. Appropriations had already been made, however, to add another unit to the two-unit Amarillo plant, and plans were underway for building a new plant of 24,000,000 cu ft capacity (later increased to 60,000,000) at Exell, Texas, in the Channing area in the southwestern part of the main Panhandle field. Additional plants were constructed later at Cunningham, Kansas; Otis, Kansas; and Shiprock, New Mexico. Four of these five plants were actually operated during the war period. The Bureau of Mines had produced a total of nearly 700,000,000 ft up to Jan. 1, 1948. In the top year, 1944, the output was 137,268,144 cu ft valued at \$872,551. Much of the war-built capacity was closed in 1945 but the output in the fiscal year 1946 exceeded 63,000,000 ft, and about 60,000,000 cu ft had been returned to underground storage in the Cliffside field. The method of recovery is to liquefy all the components of helium-bearing natural gas except helium, the residue gas being subsequently sold to local gas companies for fuel purposes.

During the interwar period, production costs at Amarillo were esti-

* After operation of three experimental helium plants, the Navy completed the construction of the first plant for production of helium, at Fort Worth, after World War I. That plant was operated by the Navy until 1925 and thereafter by the Bureau of Mines until 1929.

mated at \$7 to \$12 per 1000 ft, according to the volume produced in a given year, being naturally less when plant capacity was more fully utilized. In 1941, the prices charged to non-Government purchasers were \$9.75 for medical use, \$10.24 for scientific use, and \$11.47 for commercial use, plus service charges. Government agencies paid the Bureau of Mines only \$6.42 in that year, as no depreciation or depletion allowances could be charged.

The only known sources of low-cost helium are a few natural-gas fields in the United States, including those in the Texas Panhandle, Kansas, New Mexico, southeastern Colorado, and eastern Utah. Gas containing as much as 1 pct helium has not been found in any other country except Ontario, Canada, and there the supply is too small and rock pressures are too low for commercial production. Domestic supplies occur in formations ranging in geologic age from Cambrian to Cretaceous. The fact that the reservoirs so often lie close to crystalline rocks, however, has been interpreted as indicating that the helium may have been derived from the breakdown of radioactive elements presumably present in minerals such as pitchblende and monazite in the basement rocks. In England, helium has been made from Indian monazite, costing at least \$60 a ton and yielding only 25 cu ft of the gas. The atmosphere, too, contains helium but the proportion of helium present is so small—only one part in 185,000—that it cannot be recovered economically except as a by-product and probably never in quantities that would suffice for an air navigation program of any real magnitude.

Carbon Dioxide

At ordinary temperature, carbon dioxide is a colorless, odorless, noncombustible gas about $1\frac{1}{2}$ times as heavy as air. It dissolves readily in water and can itself be liquefied by compressing to 650 psi. Solid carbon dioxide (dry ice, Dioxide, and other forms), although it has the appearance of packed snow, weighs about $1\frac{1}{2}$ times as much as water ice, has a temperature at ordinary atmospheric pressure of -109°F (-78.5°C) or lower, and evaporates without becoming liquid. Only when the pressure exceeds about five atmospheres and the temperature is above -70°F . (the "triple-point" pressure and temperature) can carbon dioxide exist as a liquid.

Until about 1926, carbon dioxide was obtained chiefly from gases of coke ovens, lime kilns, metallurgical plants, fermentation plants, and chemical plants, but more recently increasing quantities have been produced from natural gases. In the United States, gas wells suitable for producing solid carbon dioxide are principally in Colorado, Utah, and New Mexico, although California also has been a large producer from this source. The gas occurs, as does helium, in rocks of Cambrian

to Tertiary age; the high-carbon dioxide content may be derived from oxidation of hydrocarbons with mineralized waters on the reaction of hot magmas on limestone. Mexico is one of the leading foreign producers because of the quality and persistence of the supply in the Panuco field, near Tampico. Canada, France, Germany, Italy, India, New Zealand, Japan, and probably other countries, have utilized natural sources. Gas-bearing springs have been a source of carbon dioxide in several states, notably at Saratoga Springs, New York, Manitou, Colorado, and, more recently, California. Plants for making solid carbon dioxide have been built recently in all leading countries of Europe, Japan, British India, Australia, and several Latin American countries.

Production of liquid carbon dioxide increased in the United States from 23,978 tons valued at \$2,345,743 in 1909 to 44,093 tons valued at \$6,280,647 in 1929. Solid carbon dioxide was scarcely produced at all prior to about 1925 and was commercially unimportant prior to 1929, when production jumped to around 15,000 tons. In 1933, the Census reported 58,431 tons of liquid, of which 32,250 tons was used in making solid; the production of solid was reported as 29,789 tons valued at \$1,972,130 in that year. In 1946, the net output of liquid and gas had grown to more than 110,000 tons and the makers of solid CO_2 turned out over 322,000 tons.

In 1944, when the production was about the same as in 1946, it was estimated that 80 pct of the solid product was used for refrigeration of ice cream; 15 pct for preserving meat, fish, poultry, fruits, and vegetables; and 5 pct for miscellaneous uses such as chilling aluminum rivets, shrinking cylinder liners in diesel engines, preparing blood plasma, manufacturing penicillin and making synthetic rubber. It has been used experimentally for dispelling fog at airports and for rainmaking. Cheap, abundant supplies of "dry ice" have greatly simplified quick-cooling operations in various industries—in making golf balls, oil refining, candy making, and the manufacture of varnish and sundry chemicals. It has been used to stop the flow of water during repairs to pipes and conduits, to freeze quicksands in shaft and tunnel driving, and in prospect drilling; also, to kill rats and vermin.

Liquefied gas was formerly used almost exclusively for carbonating beverages but now has become more important as a step in the manufacture of solid. Under the trade name Cardox, it is increasingly employed as a safe, slow-acting explosive. The gas is employed as refrigerant in mechanical refrigerating machines although generally considered less satisfactory for this purpose than ammonia, sulphur dioxide, Freon, or methyl chloride. Both solid and liquid CO_2 are used extensively in fire extinguishers and the bottled gas is convenient for inflating tires, rubber rafts, and all sorts of collapsible molds in factories.

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CHAPTER 30

MONAZITE

BY JOHN B. MERTIE, JR.*

MONAZITE formerly was described as moribund, but, in the light of recent developments, it is no longer so. It is the common source of the rare earths and thorium, both of which are becoming progressively important in industrial and other applications. Moreover, by the action of foreign governments, the sources on which the United States has depended for its supply are now either restricted or cut off entirely. Monazite has thus become a scarce mineral and processors in this country are endeavoring to acquire it from all available sources.

RARE EARTHS AND THORIUM

The rare earths proper, as defined by spectroscopists, are the oxides of cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutecium, with atomic numbers ranging respectively from 58 to 71. Chemists include with the rare earths scandium, yttrium, and lanthanum, with atomic numbers respectively of 21, 39, and 57. Thorium, with an atomic number of 90, is analogous to lanthanum, in that it precedes a second group of elements, whose oxides constitute the "rare earths of higher order." These are protactinium, uranium, neptunium, plutonium, americium and curium, with atomic numbers ranging respectively from 91 to 96. The last four mentioned are artificially prepared elements that so far have not been detected in nature.

The rare earths with odd atomic numbers, except europium and lutecium, have no natural isotopes; and the two exceptions have only two isotopic forms. Those with even atomic numbers have from 4 to 7 natural isotopes. Samarium¹⁴⁸ is radioactive, disintegrating over a half-life of 1.4×10^{11} years with the emission of alpha rays. Lutecium¹⁷⁶ is weakly radioactive, disintegrating over a half-life of 2.4×10^{10} years, with the emission of beta and gamma rays. At least 64 radioactive isotopes of the rare earths proper have been artificially prepared.

Thorium is a strongly radioactive element, with a half-life of 1.39×10^{10} years, which disintegrates through a series of 14 isotopes of 10 elements. The two longest lived and most important of these are

* Geologist, U. S. Geological Survey, Washington, D. C.

radium²²⁸, known as mesothorium 1, which has a half-life of 6.7 years and disintegrates with the emission of beta rays; and thorium²²⁸, called radiothorium, which has a half-life of 1.90 years and discharges alpha and gamma radiation. Thorium²³² is the principal natural isotope found in nature; but thorium²²⁸ and all the other disintegration products also occur with it.

CHARACTERISTICS OF MONAZITE

Monazite is a mineral of mystery. It is a monoclinic phosphate of the rare earths, with the general formula XPO_4 , but it contains also from zero to 20 pct, commonly 4 to 10 pct, of thoria. Analyses show the presence of silica in amounts ranging from very small quantities to 10 pct and also of numerous other nonradioactive elements. The radioactive elements that result from the disintegration of thorium are necessarily present, as is also a stable form of lead, Pb^{208} . Uranium also occurs commonly in small amounts, associated with thorium, for which reason its decomposition products are also present. Probably it is no accident that all these elements occur in one mineral, and it is possible that they may be the products of some process of natural fission that occurred in the remote past.

The rare earths are divided chemically into three groups known as the cerium, terbium and yttrium earths. Cerium, lanthanum, neodymium, and praseodymium, of the cerium earths, are the usual rare-earth elements in monazite. Samarium, of the same group, is less commonly present, and promethium, though first detected in monazite, is exceedingly scarce. Some of the elements of the terbium and yttrium groups may also be present but ordinarily not all of them. Scandium is rarely present.

Monazite occurs in placers as honey yellow to greenish yellow resinous grains, some of which are iron-stained to reddish brown and are opaque. The hardness ranges from 5 to 5.5 and the specific gravity from 4.9 to 5.3. Monazite has one perfect cleavage parallel to (001), a good cleavage parallel to (100), and one or more less perfect cleavages or partings. The mean index of refraction ranges from 1.785 to 1.805 and the birefringence from 0.045 to 0.055. The optic angle is small, varying from 5° to 15° . Though listed as weakly magnetic, monazite ranges from grains that are held with difficulty in a field of 5000 gauss to others that are almost ferromagnetic. This magnetism is an atomic property of the rare earths that is unrelated to the presence of iron. Monazite is a poor electrical conductor.

If it contains neodymium, monazite can be identified invariably by examining it in reflected sunlight with a hand spectroscope. A strong absorption band will be seen in the yellow and a fainter one in the green. The presence of erbium will also cause an absorption in the

green. Owing to its brittleness, monazite may be cracked between the teeth, which provides a crude test. The radioactivity as determined by an electroscope yields another confirmatory test.

OCCURRENCE OF MONAZITE

United States

Monazite in small amounts is common in some granite, granite gneiss, and related pegmatites, and therefore has been described from many localities throughout the world. It is reported as a primary mineral from many of the eastern states from New England to Georgia; from the Black Hills, Arkansas and Texas; and from a number of western states in the Cordilleran province. Commercial deposits, however, both in this country and abroad, are restricted almost entirely to placers.

The only placers in the United States that have been worked primarily for their content of monazite are in North and South Carolina. They are derived from a slightly gneissoid granite, from granitized gneiss, and from related pegmatites that crop intermittently southeast of the Blue Ridge, in a belt 200 miles or more long and 15 to 20 miles wide. The pegmatitic veinlets have a higher tenor in monazite but the granite and granitized gneiss, because their volume is far greater, are the principal bedrock sources.

The Idaho batholith contains a small percentage of monazite but no placers have been found that are workable for their content of this mineral alone. Gold placers, however, within the area of the batholith yield concentrates that are potential sources of monazite.

Present and ancient beach sands along and near the east coast of Florida have been mined for some years for their content of ilmenite, rutile, and zircon and these sands contain also a small percentage of monazite, which evidently was transported to Florida by ancient streams that drained southeastward from the Carolinas, and by shore currents.

FOREIGN COUNTRIES

Commercial deposits of heavy minerals derived principally from granitic rocks are known in India, Brazil, Australia, Ceylon, Netherlands Indies, Malaya, Egypt, Korea, Formosa, and Norway. All of these, except the monazite from Norway, are heavy sands, which contain zircon, ilmenite, rutile, garnet, monazite, and other heavy minerals, in widely varying proportions, so that monazite is only one of the minerals that are recovered from such placers.

The most important of these are the littoral sands that occur intermittently along the southwest coast of India, in the state of Travancore, from Cape Comorin northwestward for more than 100 miles to Trikunnappuzha. Monazite-bearing sands of lower grade occur also

east of Cape Comorin in the Tinnevely district and also near Walthair in Vizagapatam. Most of these deposits are localized near the mouths of streams. The primary sources are granite and related pegmatite that occur inland but an important secondary source is the Warkalay formation, of late Tertiary age, which commonly crops close to the beach deposits. Sand dunes back from the beach also contain the heavy minerals. These Indian sands are fine grained and the monazite is well concentrated for the market. In general, the content of thoria is higher than that of the Brazilian monazite.

Next in importance are the beach deposits along the coast of Espirito Santo, Bahia, and Rio de Janeiro, in Brazil. These occur along the present beaches, on elevated beaches inland from the coast, and along the bars of streams that transect and erode the beach deposits. Granites, granitic gneisses and related pegmatites are the original sources.

The Australian deposits occur intermittently along the Pacific beaches, from Port Macquarrie, New South Wales, northward for 250 miles to the Queensland border, and for a considerable distance in Queensland. They are particularly abundant between the Clarence and Richmond Rivers. The primary sources are granite and pegmatite in the New England and Copley districts to the west.

Monazite-bearing beach sands occur along the west coast of Ceylon from Colombo northward for 130 miles to Mannar and south and east from Colombo for 140 miles to Hambantota. Fluvial placers occur inland. The thoria content of the monazite, however, is reported to be only 4 pct.

The Netherlands East Indies began in 1936 to produce a heavy mineral concentrate, from which monazite is now being recovered. On the Malaya peninsula, monazite occurs in the cassiterite placers.

A new deposit was opened during the war at the mouth of the Nile River, in Egypt, near Rosetta and Damietta. The principal heavy minerals of these sands are ilmenite, zircon and monazite.

Pre-Cambrian and Cretaceous granitic rocks that contain monazite, zircon and fergusonite are widespread in Korea and probably extend northward into Manchuria. These rocks have produced many monazite-bearing fluvial gold placers that have been worked for more than 50 years, but the monazite was not saved. Similar but shallower beach deposits occur along the central part of the east Korean coast, facing the Sea of Japan.

In Norway, a very small amount of monazite is recovered as a by-product of the hard-rock mining for feldspar.

PRODUCTION AND ECONOMIC CONTROL

Monazite was mined in the Carolinas from 1887 to 1911 and again in small amounts from 1915 to 1917. The total recorded production dur-

ing these two periods was about 5462 short tons, with maxima of 786 tons in 1895 and 676 tons in 1905. The Brazilian deposits were found in 1895 and their richness caused a slump in American mining in 1896 and 1897, but from 1898 to 1910 the average annual output was only 376 tons. The discovery of the Indian deposits in 1909, however, coupled with their higher content of thorium and the availability of cheap labor, soon put an end to the American monazite-mining industry, though small amounts were recovered in Florida in 1925 and also in recent years as a by-product of the mining of ilmenite, rutile, and zircon.

An attempt was made years ago to save and refine the dredging concentrates of the Boise Basin, Idaho, for their content of monazite, but the concentrating plant burned and the project was abandoned. Arrangements have been made recently, however, to recover monazite from placer concentrates in the Warren district, Idaho.

Brazilian production reached its peak of 7121 tons in 1909, after which it diminished, becoming nil for 1934, 1935 and 1936; it is now increasing, with a production in 1943 of 1550 tons. The Indian output reached a peak of 2371 tons in 1918 and then declined rapidly, but since 1930 the production has steadily increased, reaching 5847 tons in 1938.

Most of the monazite imported into the United States in recent years has come directly or indirectly from India; smaller amounts have come from Brazil. Early in 1947 the Rajah of Travancore placed an embargo on the export of monazite from his state but a few months later he contracted to supply the British Government with a large tonnage. The Brazilian Government, also in 1947, took steps toward the nationalization of its deposits, so that the amount that may be exported is now under government control. The United States, as of 1949, requires several thousand tons of monazite annually, and possibly considerably more, and finds this amount hard to obtain. Hence monazite has now become a scarce and critical mineral commodity.

The price of monazite has varied greatly over the years but just prior to the present shortage it was quoted nominally at \$60 a ton, though processors in this country were able ordinarily to buy it for two thirds of that price. The price in March 1949 was \$230 a ton.

USES

Carl Auer, Baron von Welsbach, the Austrian scientist, patented the Welsbach gas mantle in 1885. Thereafter for 25 years monazite was used mainly for its content of thorium, but the introduction of the tungsten lamp about 1911 soon rendered the gas mantle obsolete in the United States. A thriving trade in gas mantles for foreign countries still persisted but the use of thorium for this purpose gradually declined.

Thorium is now used mainly in other applications, but the rare earths are more needed in industry than is thorium. As a result of these conditions, the commercial specifications for many years required a stated content of thorium in monazite, originally 6 pct and later 8 pct, but in recent years the specifications have been changed to read 57 to 60 pct of the rare earths. Another result has been that the processors have accumulated large stock piles of residues containing thorium and the less used rare earths.

At present, about half of the monazite is processed for use as cerium fluoride, nitrate and oxide, in the cores of carbons required for motion-picture projectors, floodlights, searchlights, and therapy lamps. Pyrophoric alloys of the rare earths with iron or aluminum use perhaps one fourth in the manufacture of gas and cigarette lighters. Some of the alloys are ferrocerium, Misch metal, Auer metal and Kunkeim, the last three containing other rare earths besides ceria. Some of these, and also other alloys, are used in metallurgical applications. Cerium acetate is used for rendering fabrics waterproof, mothproof and mildewproof, and cerium, neodymium and praseodymium are utilized in the manufacture of special glazes and glasses. The rare earths are used for printing and dyeing fabrics and as a glass-polishing compound.

Lanthanum, in combination with tantalum and tungsten, is used by the Eastman Kodak Co. to make a nonsiliceous optical glass of high refractive index and low dispersion. Under certain conditions, yttrium may be substituted for lanthanum. Neodymium and praseodymium are required for coloring glass and other products and the two unseparated (didymium) are used in special blue glasses supplied to glass blowers to protect their eyes against intense sodium light. Lanthanum and erbium are used in beauty preparations. Chemical compounds of the rare earths are required also in other industrial applications.

Thorium and its compounds are used mainly in the filaments of tungsten lamps; for electron-emissive purposes, as in radio tubes; for refractories resistant to high temperature; for gas mantles, and as catalysts. Radium²²⁸ (mesothorium 1) is refined chemically from natural thorium and, being cheaper than radium²²⁶, is used for luminous watch dials, and for other purposes where the substitution may be made.

A new use for thorium, which cannot yet be evaluated, is its application in the production of nuclear power. It is reported to be directly fissionable by fast neutron rays but under bombardment by slow neutrons produces thorium²³³, which disintegrates with beta and gamma radiation into protactinium²³³. The latter disintegrates with beta and gamma radiation into uranium²³³, which has a half-life of 1.63×10^5 years, and is fissionable. All these reactions, however, require an outside source of neutron radiation.

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CHAPTER 31

NATIVE BITUMENS

By A. H. REDFIELD*

BITUMENS have been defined by Abraham¹ as substances of variable color, hardness, and volatility; composed principally of saturated hydrocarbons, substantially free from oxygenated bodies, sometimes associated with mineral matter; the nonmineral constituents being fusible and largely soluble in carbon disulphide. The principal bituminous substances other than petroleum known to commerce are: (1) native asphaltites, such as gilsonite, grahamite, and glance pitch, distinguished by their hardness and relatively high fusing point; (2) native asphaltic pyrobitumens, such as wurtzilite, distinguished by their infusibility and comparative insolubility in carbon disulphide; (3) mineral waxes, such as ozokerite, distinguished by their high content of crystallizable paraffins; (4) native asphalts, containing varying amounts of mineral matter, distinguished by the comparative absence of crystallizable paraffins; and (5) bituminous residues obtained from the distillation of petroleum.

GILSONITE

Gilsonite, a black native asphaltite 98 to 99.9 pct pure, characterized by a hardness of 2 (Mohs), a specific gravity of 1.01 to 1.10, and melting point of 230° to 400°F (K and S), is mined commercially only in northeastern Utah. It occurs in parallel, almost vertical veins, from a few inches to 18 ft wide and 8 to 30 miles long, that cut across the Tertiary limestone and shale of the broad Uinta Basin. The bitumen is believed to have been distilled by heat from oily material in the underlying Green River shale.

At the Rainbow mine of the American Gilsonite Co.,† the gilsonite, formerly extracted in an opencut by a system of slopes and benches, is now mined by shafts and horizontal drifts. Little timbering is required. The mining methods of the Raven Mining Co., Chicago, and of the American Asphalt Association and the Utah Gilsonite Co., both of

* Petroleum Economics Division, Bureau of Mines, Washington, D. C. The information is published by permission of the Director, Bureau of Mines, U. S. Dept. of the Interior.

† Properties of Gilson Asphaltum Co. (Barber) were transferred on January 1, 1946, to American Gilsonite Co., jointly owned by Standard Oil Co. (California) and Barber Asphalt Corporation.

St. Louis, are equally simple. To avoid dust explosions and shattering of ore, explosives are little used. The brittle gilsonite is dug out with picks, hand-selected, sacked, and hoisted to the surface.

"Select gilsonite" and "jet asphaltum" are used principally in the manufacture of varnishes and japans, printing and rotogravure inks. "Standard gilsonite" is employed in the manufacture of storage-battery cases and molded articles, brake linings, floor tile and mastic, sealing compounds, insulation, and wood stains. Weathered gilsonite from the surface is used to saturate roofing felt and for blending with rubber.

Sales of gilsonite by producers averaged 34,000 short tons a year from 1935 to 1941 but rose during the war and attained 68,407 tons in 1946. The value, f.o.b. mine or shipping point, increased from \$20.96 per short ton in 1935 to a peak of \$28.24 in 1939 but declined during the war and postwar periods to \$20.47 in 1946.

WURTZILITE

Wurtzilite, commercially called "elaterite," is an asphaltic pyrobitumen characterized by a hardness of 2 to 3, by a specific gravity of 1.05 to 1.07, and by its infusibility. It occurs in narrow veins, 1 to 22 in. wide, 100 ft to 3 miles long, that cut the Tertiary beds of the Uinta Basin of northeastern Utah. It is mined 50 miles southwest of Fort Duchesne, Utah, by the Raven Mining Co. of Utah, Chicago, Illinois, by horizontal drifts and slopes.

Crude wurtzilite—an insoluble, refractory mixture of hydrocarbons—is heated under pressure from 500° to 580°F. The vapors evolved are condensed and returned to the still, where they reduce the material to a plastic mass, which, after heating, is converted to a substance soluble in carbon disulphide and moderately soluble in 88° naphtha, known as "Kapak," or wurtzilite asphalt. Wurtzilite asphalt is used in the manufacture of paints and coatings for weatherproofing and preventing corrosion, for electrical insulation, and for blending with rubber.

From 61 short tons in 1935, sales of wurtzilite rose to a peak of 133 tons in 1937 and declined to 11 tons in 1944. None was sold in 1945 and only 24 tons in 1946. From 1936 to 1944, the average sales price of wurtzilite varied between \$77 and \$80 per short ton. In 1946, it was sold at \$44.42 per ton.

GRAHAMITE AND GLANCE PITCH

Grahamite, an asphaltite with a specific gravity of 1.15 to 1.20 and a fusing point of 350° to 600°F (K and S), was mined in Pushmataha County, Oklahoma, until 1924 and formerly in Ritchie County, West Virginia.

In Cuba, veins of grahamite and glance pitch, cutting a complex of sedimentary and serpentinous rocks, have been mined by American,

British, and Cuban companies. At Mariel, in Pinar del Rio, nearly vertical veins of grahamite 6 to 30 ft wide and 300 ft long are mined by horizontal crosscuts and drifts and stoped out by manual labor. The crude material, 55 to 588 pct pure, with a specific gravity of 1.49 and a melting point of 374° to 400°F, is picked, hoisted, and sacked either in crude form or after steam refining. At Talaren, in Camaguey, a steep vein of glance pitch with a specific gravity of 1.12, a hardness of 2, and a fusing point of 315° to 345°F, has been mined by shafts, drifts, and slopes. Exports of grahamite and glance pitch from Cuba, chiefly to the United States and the United Kingdom, amounted to 8391 short tons in 1936 but declined to 1064 short tons in 1943 and 110 tons in 1944. From 1942 to 1944, approximately 104,000 tons of low-grade grahamite was burned in Cuba to ease the fuel shortage.

The United States imported 6692 short tons of grahamite from Cuba in 1945 but only 315 tons in 1946.

OZOKERITE

Ozokerite, a native wax believed to have been derived from the polymerization of paraffin-base petroleum, has long been mined in Galicia, along the overthrust front of the Carpathian Mountains. Rich veins of ozokerite filling fractures in Oligocene and Miocene beds have been mined by shafts and galleries in the districts of Drohobycz and Stanislawow. These districts were occupied by the USSR late in 1939 and passed from Polish to Soviet sovereignty at the end of World War II. No statistics of ozokerite mining in Galicia have been available since 1935.

Prior to 1929, ozokerite was mined near Soldier Summit, Utah, by the Ozokerite Mining Co., Inc. After suspension of operations for many years, a small tonnage was mined by the company in 1946.

LAKE ASPHALT

In southwestern Trinidad, at Brighton, a lake of natural asphalt, which covers approximately 114 acres and is nearly 300 ft deep at the center, has been worked for years by the Barber Asphalt Corporation, of Philadelphia. This emulsion of bitumen, water, mineral, and vegetable matter is believed by Richardson to be derived from heavy asphaltic oil in the underlying Miocene in contact with colloidal clay and silica. Crude asphalt, which contains 33 pct of water and 27 pct of mineral matter, is dug by manual labor from the surface of this lake, loaded into cars, and hauled by cable to the refinery, where it is dehydrated in open tanks and heated by steam. Some crude asphalt is transported in bulk cargoes to the United States, where it is refined for domestic uses.

Refined Trinidad asphalt has a specific gravity of 1.4, a hardness of

1 to 2, and a softening point of 183° to 189°F (K and S). It contains 54 to 56 pct of bitumen, 38.5 pct of colloidal clay and silica, and 4 pct of water of hydration. It is used for paving and for the manufacture of roofing, waterproofing, mastic, molding compounds, pipe coatings, insulation, and paints. Production of lake asphalt in Trinidad declined from 163,412 short tons in 1937 to 70,692 tons in 1945. Of the 1945 production, 31,360 tons was exported. The United States received 4926 short tons of lake asphalt from Trinidad in 1945 and 3943 tons in 1946.

BITUMINOUS ROCK

In west central Kentucky, extensive deposits of bituminous sandstone occur in Edmonson, Breckinridge, Grayson, and Hardin Counties in the Chester formation (upper Mississippian) and the Pottsville formation (Lower Pennsylvanian). The asphalt is believed by Russell²⁹ to be derived from petroleum, altered by the oxygen contained in circulating waters. At Kyrock, Edmonson County, the Kentucky Rock Asphalt Co. of Louisville mines the bituminous Pottsville sandstone throughout the year in large open pits. After being crushed, pulverized, mixed by machinery and delivered by conveyor belts to barges, the rock is floated by river to Bowling Green or Rockport. At Summit, Hardin County, the bituminous Chester sandstone is quarried by the Ohio Valley Rock Asphalt Co. of Louisville. It is crushed, pulverized, and loaded directly into open-top gondola cars, from which it may be unloaded by steam shovels or picks and shovels.

The prepared material, which contains 7 pct of bitumen, may be laid cold to surface highways, railroad platforms, bridge floors, and tennis courts. Nearly half of the rock asphalt is sold directly to states, counties, and municipalities.

In northern Alabama, at Margerum, the Alabama Asphaltic Limestone Co., of Birmingham, mines a Middle Mississippian oölitic limestone in open quarries. The rock, which contains 2.5 to 9.5 pct of bitumen, is crushed and milled, fluxed with petroleum asphalt, and sold for paving purposes.

In Uvalde County, Texas, an Upper Cretaceous coquina limestone that contains 9 to 12 pct is drilled and blasted down in open pits by the Uvalde Rock Asphalt Co. and White's Uvalde Mines, both of San Antonio. It is crushed, pulverized, blended with asphaltic flux oil, and shipped by rail in open-top cars. The prepared material, which averages 10 pct of asphalt, may be laid cold to surface highways. Floor tiles and plastic planks are made with the extracted bitumen.

In the Arbuckle Mountains of south central Oklahoma, nearly horizontal beds of Ordovician bituminous sandstone and limestone are quarried along the face, crushed, mixed and sold for paving purposes by the Southern Rock Asphalt Co., of Oklahoma City.

In Carbon County, Utah, a seam of Tertiary sandstone 1300 ft thick, containing 9.5 to 12.0 pct of bitumen, outcrops for 17 miles along the upper sides of Sunnyside Canyon. It is mined by the Rock Asphalt Co. of Utah in open cuts. The rock is blasted down, crushed, transported $3\frac{1}{2}$ miles by aerial tramway and $2\frac{1}{2}$ miles by motor trucks to a mill, where it is pulverized and screened. It is shipped by rail and is used for surfacing highways.

At Vernal, Uintah County, Utah, a small tonnage of bituminous sandstone is extracted by the county road department for surfacing the county highways.

Rock asphalt was produced in 1946 in California and Missouri.

In northern Alberta, along the banks of the Athabaska River, Lower Cretaceous bituminous sands, 100 to 200 ft thick, are exposed for 70 miles above and 35 miles below Fort McMurray. From 1931 to 1938, the sand, containing 12 to 20 pct of bitumen, was processed at Bitumont, Alberta, for paving asphalt and 1057 bbl of fuel oil was extracted. In 1941 and 1942, the sand was mined by Abasand Oils, Ltd., and treated with hot water to extract crude petroleum, which was refined in a small distillation plant into commercial products. About 35,000 short tons of sand was treated and 30,000 bbl of crude petroleum extracted. On April 1, 1943, the Dominion Government leased the properties with an option to buy but a fire destroyed the separation plant and an official report declared the entire project uneconomical.

COMPETITION WITH PETROLEUM ASPHALT

In all of their industrial uses, native bitumens and rock asphalt compete with asphalt manufactured from petroleum. To the advantages of large-scale production and extensive marketing organization enjoyed by petroleum asphalt, the native asphaltites have opposed the advantages of their physical characteristics for special uses and bituminous rock its availability for immediate laying.

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CHAPTER 32

NITRATES AND NITROGENOUS COMPOUNDS

BY HORACE R. GRAHAM*

CHEMICAL nitrogen and the "nitrates" of commercial significance are derived mainly from three basic sources: (1) the natural deposits in the form of nitrate-bearing earth and clay, which, being largely water-soluble, can exist only in the most arid portions of the earth; (2) coal, which yields not only nitrogen but also the additional by-product hydrogen required for the synthesis of ammonia and its compounds; (3) the atmospheric air, which contains 75.5 pct by weight of pure nitrogen gas.

NATURAL NITRATE DEPOSITS

Occurrence

Although natural nitrate deposits consisting principally of the salts of sodium and potassium have been reported in Egypt, South Africa, Mexico, Argentina, Colombia, Peru and the USA, the only known natural nitrate resources of commercial importance are the vast deposits found in the Atacama, Tarapaca and Antofagasta regions of northern Chile, lying in a narrow strip 10 to 50 miles wide and roughly 450 miles long, between latitudes 19° and 26°S. In addition to yielding nitrates of sodium and potassium, these deposits are the source of the major portion of the world's supply of iodine.

The nitrate-bearing ores known in Chile as *caliche* are variable in composition and may contain from 5 to 30 pct each of nitrate, chloride and sulphate. While the deposits are present chiefly in the form of the sodium salt, potassium, magnesium and calcium also occur in percentages from 0.1 to 5; usually as double salts with sulphate, which are but slightly soluble in nitrate leach solutions. These double salts are bloedite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$), glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$), polyhalite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Some deposits contain up to 30 pct of their ni-

* President, Lautaro Nitrate Co., Ltd.; President, Compania Salitrera Anglo-Chilena, New York, N. Y.

The author wishes to thank Mr. P. F. Kruger, First Executive Vice President in Santiago, Chile; Mr. G. F. Coope, formerly Assistant Administrator; Dr. E. S. Freed, Research Director, of the Lautaro Nitrate Co., Limited, and the Compania Salitrera Anglo-Chilena; and Mr. H. L. Tower, Engineer of Anglo-Chilean Nitrate Corporation, for aid in compilation of the data in this chapter.

trate content in the form of a double salt called Darapskite ($\text{NaNO}_3 \cdot \text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$), which is insoluble in cold leach solutions but is completely decomposed and soluble at elevated temperatures; i.e., 55°C and higher. Minor salts such as potassium perchlorate, sodium iodate and unknown borate materials, exist in percentages from 0.02 to 1. The water-insoluble salts may vary from 20 to 80 pct in the nitrate minerals.

The physical characteristics of the ore are variable. Color ranges from pure white to browns and reds and there are occasional samples of yellow, black and blue. Nitrate minerals occur in slimy, sandy or gravelly form, dependent upon the preponderance of the constituents that are cemented with salts to form a hard conglomerate.

Genesis and Distribution of Chilean Deposits

No acceptable explanation of the primary origin of the nitrate minerals in Chile has been developed but it seems definite that nitrate was finally collected in an inland sea, which eventually deposited part of its load along its shore lines. Finally the sea drained into the Pacific Ocean, but the deposits that had been laid down on the eastern shore were either dissolved or washed away by drainage from the Andes, or covered by alluvial debris, leaving the present deposits on the western shore of the inland sea or the eastern slope of the coast range.

The typical deposits occur on the comparatively low, level slopes on the east side of the coast range, and consist of a layer varying from a few inches to several feet. Above the nitrate mineral layer lies an overburden varying through the same ranges of thickness and composed of material from loose sand and dust to a firm conglomerate of rock fragments and salts. These deposits are extremely irregular in shape and of spotty location. A large proportion of the original nitrate undoubtedly has been leached from the ground by heavy rains, which occur about every 10 years, but several hundred million tons of recoverable nitrate still remain for exploitation.

One of the best descriptions of the probable genesis of the nitrate deposits may be found in the admirable work published in 1919 by Professors Benjamin L. Miller and Joseph T. Singewald,³² in which they say:

"Most of the theories that are or have been in vogue to account for the Chilean nitrate deposits may be grouped under four headings, according to the manner in which the nitrate is supposed to have been formed. These are: (1) the seaweed theories, (2) the guano theories, (3) the bacterial theories, (4) the electrical theories.

"The seaweed theory was proposed in 1867 by Dr. C. N. Noellner. He believed that great quantities of seaweed collected along the portion of the west coast paralleled by the nitrate fields, due to the prevailing westerly winds, and that occasional hurricanes piled this up. An uplift

of the land or a recession of the sea followed. The sea water that remained behind evaporated and furnished the sodium chloride and the nitrate resulted from the slow oxidation of the seaweed.

"In 1860, C. C. Hillinger advanced the theory that the nitrates are due to extensive deposits of guano that covered the banks of a large saline sea. The saline waters flooded the guano and reacted with the nitrogen to finally form sodium nitrate. Very similar is the theory proposed in 1894 by A. Gautier. He derives the nitrates from bird guano in the form of calcium nitrate. This was then liquefied little by little by the night dews, and thus brought into contact with the salt of the salares, basin-like depressions in the pampa characterized by an abundance of sodium chloride, where it was converted into sodium nitrate. The most detailed presentation of this theory was made in 1910 by R. A. F. Penrose, Jr. He believes the nitrate region was once part of the ocean bottom, and finally an interior basin occupied by salt lakes. Guano beds deposited about the borders of these lakes furnished nitrates that were carried down into their waters.

"The way for the bacterial theory was paved in 1862, when Pasteur suggested that the oxidation of the nitrogen compounds in the soil is accomplished by living organisms. The best presentation of this theory is that by Dr. William Newton, in 1896. He ascribes the genesis of the nitrate to the action of the nitrifying organisms on ancient vegetable matter in the soil of the region. The nitrates, thus formed, he says, have been collected by the drainage waters of the entire region, and gathered and evaporated at the site of the present nitrate deposits, which is the point where these waters are stopped by the coast line of hills. As thus developed, this is one of the most plausible theories that have been advanced.

"The electrical theory was advocated in 1903 by Dr. Semper, and in the following year, by Semper and Michels in their paper on the nitrate deposits. According to the more prevalent form of this theory, the nitrates are formed by the oxidation of the nitrogen of the air through the electrostatic tension that is such a marked accompaniment of the frequent coast fogs, or *camanchacas*, that roll in over the nitrate pampa at night.

"An atmospheric source of nitrates that has received less attention, is that formed during electrical storms in the Andes. This has certainly been at least a contributing factor to the nitrate supply of the region.

"Sundt believes that the nitrates have been formed in situ by the decomposition of feldspathic porphyries which yielded sodium carbonate, later transformed into sodium nitrate by the action of nitric acid contained in the atmosphere. He states that the deposits are only found where these high sodium rocks occur.

"Briefly put, the authors believe that the nitrate deposits have re-

sulted from the accumulation, by means of evaporation, of the minute nitrate content of the underground waters of the region. In other words, they represent a sort of efflorescence of soluble salts out of the ground-water. This accumulation has been made possible through the remarkable relations of ground-water and climate existing in the region of the nitrate deposits.

"The pampa has been built up with loose detrital material washed down mainly from the slopes of the Andes on the east. Through such material, capillarity is very effectively feeding the shallow ground-water in enormous quantity to the atmosphere through evaporation. Whatever soluble salts this ground-water is carrying are left behind to accumulate in the soil between the surface and the ground-water level.

"There is a constant flow of ground-water from the regions of more abundant precipitation in the higher slopes of the Andes on the east, westward beneath the pampa, toward the sea. The pampa has a gentle westward slope to the foot of the Coast Range, where the presence of these mountains causes an abrupt rise in the topography. Since the surface of ground-water follows in its general outlines the overlying topography but is less accentuated than the latter, the ground-water level should lie nearest the surface on this western edge of the pampa; and consequently here should take place the maximum evaporation, and for that reason, the maximum accumulation of soluble salts.

"The richest nitrate ground is frequently that immediately contiguous to the "salares," and the nitrate tends to decrease in quantity with increasing distance and elevation above the salar. There are often small knolls within a salar and these also carry nitrate above its level.

"The fact that the nitrate occurs around and not in the salares is easily understood, in view of the deliquescent nature of this substance. Suppose that salt and nitrate had accumulated in these depressions, when a rain did come, or when the pampa was deluged, as it occasionally is, by torrents bursting down from the Andes, these would be the places for the waters to collect before they had been completely dissipated through seeping into the soil and by evaporation. They would be the wettest places and the last places to remain wet. Whatever nitrate existed there would be taken into solution, and it would at once begin to effloresce out of the boundaries of the salar, as, for instance sal ammoniac crawls out of its solution in the La Clanche cell, and accumulates in the dry ground surrounding it. This process repeated at intervals would keep the salar free of nitrate, and leave the accumulation of salt behind.

"If there is or has been an unusual activity in the generation of nitrates in this region, as the authors of the older theories have felt it necessary to assume, it merely means that it has taken less time to accumulate the present deposit than if there had been no such unusual activity.

"The only feature in which this region might be unique in the generation of nitrates is that apparently more processes have been active here than is generally the case in other places. There is no evidence to show that any one of the possible sources would be adequate to account for all of the nitrate, and we believe that all combined would be inadequate, if it were not for the all important remarkable conditions of climate, underground waters, and geologic structure existing in this region.

"Former attempts to satisfactorily explain these deposits have failed because undue emphasis has been laid on the mode of generation of the nitrates whereas the fundamental explanation lies in the conditions that have made possible their accumulation."

Prospecting and Mining Practice

Inasmuch as the caliche is usually found close to the surface, and in relatively small thicknesses, prospecting and exploration are rather simple. The present practice is to sink pits one meter in diameter in promising localities and cut a good-sized sample channel vertically in each, sectionalizing the samples according to the variations in the ground, so as to get as good a classification of overburden, ore and underlying material as possible. Pits are first sunk at wide intervals—perhaps 500 meters or even 1 kilometer—and then at closer intervals when promising areas are found.

Both hand mining and mechanical mining are used; the former in most Shanks-process plants, which demand a high-grade ore. In hand mining, the ore and overburden are blasted together, usually by hand-drilled holes, although sometimes air drills are used, then the miner selects the ore and breaks it into pieces of convenient size, which he places upon a carefully squared-up pile for measurement and hand-loading into cars for shipment to plant. A variant of this is underground mining of beds of high-grade caliche lying under overburden of thicknesses up to 10 or 12 meters. Methods similar to hand mining are used, modified to suit conditions.

For the new Guggenheim plants, the mechanical mining system is briefly as follows (Fig 1): A loop system of electric haulage is laid out, in which main lines are electrified and shifting mining lines are not. Combination battery trolley 36-ton General Electric locomotives are used for ore haulage. Each mining section is equipped with a Bucyrus Erie 100-B electric shovel and a similar dragline. A mining section includes about 2000 meters of length between the empty line and the load line, and usually is laid out with a favorable grade for the loaded ore trains, which operate on storage battery through these sections. The dragline removes the overburden over a cut 14 meters wide, casting it into the previous cut. Part of the overburden requires blasting. Ore is then drilled and blasted and the shovel follows down the cut, loading

into the ore cars. Track, airline and powerline towers are shifted as the cuts progress.

Extraction of Nitrate and Preparation for Market

Sodium nitrate is now extracted from caliche in two types of plants. Until 1926, the only extraction plants in operation, of which about 150 were in existence, were known as the Shanks plants or *Oficinas*. In Shanks Oficinas, the caliche is brought from the mine, known as the pampa, in small cars up to 10 tons capacity, and crushed in jaw crushers to about 2½-in. maximum size and finally is delivered to boiling tanks

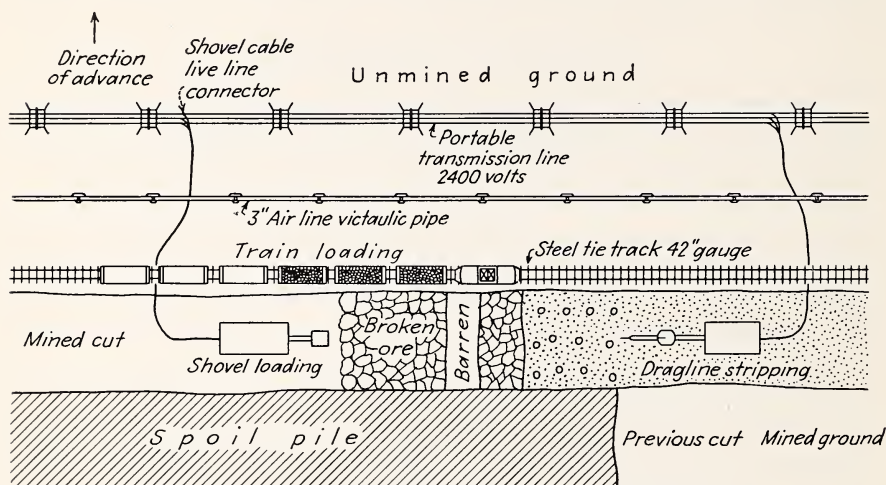


FIG 1—PLAN FOR MINING NITRATE ORES WITH POWER SHOVELS.

of 50 to 90 tons capacity. In these tanks, the caliche is leached at the boiling temperature with a mother liquor containing about 450 grams per liter of nitrate. By contact with the caliche at the boiling temperature for 12 to 15 hr, the mother liquor dissolves more nitrate to bring the nitrate concentrations up to about 700 grams per liter. The strong solution is then run to a settling tank, to settle out the slimes, and finally the clear hot solution is run to large open tanks for cooling.

The residue in the boiling tanks is washed with a series of graduated washes and finally with water, and after draining is discharged by hand into small cars beneath the boiling tanks and hauled to waste. The residue contains from 3 to 8 pct sodium nitrate, depending upon the slimy characteristics of the caliche.

The strong solution, after about 8 days cooling, is again reduced to mother liquor for use in a new cycle of operations. The crystal deposit of nitrate, after the mother liquor is drained off, is shoveled into small cars and dumped onto a storage yard for further drainage, and in about three months is ready for bagging and shipping. This nitrate is of 95.5

to 96 pct purity, and contains 1 to 2 pct moisture and small amounts of sodium chloride, sodium sulphate, borax, potassium perchlorate, iodine (as iodate), and other salts valuable to the development of plant life.

The capacities of these Shanks Oficinas vary from 10,000 to 110,000 tons of sodium nitrate per year and in them caliche of less than 13 pct sodium nitrate cannot be treated economically.

In 1926 and 1930, two new large plants, known as Maria Elena and Pedro de Valdivia, were built to use a new process, known as the Guggenheim process, each to produce more than 500,000 tons annually. In this process, the caliche is mined by power shovels and the mining re-

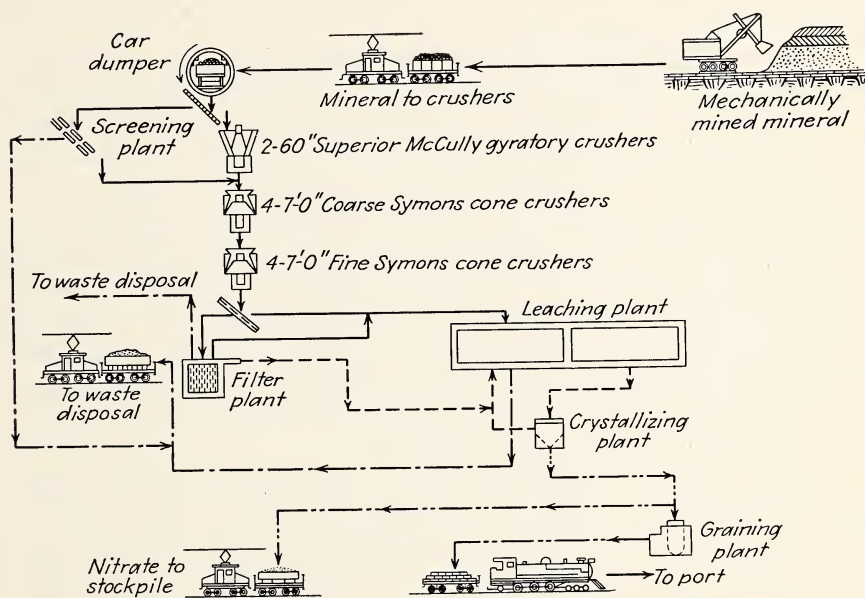


FIG 2—FLOWSHEET OF GUGGENHEIM MECHANICAL PLANT.

covery from the deposits is nearly 100 pct of the nitrate content, but the average sodium nitrate content of the caliche is reduced to about 8 pct. The new Guggenheim process is particularly designed for treating low-grade mineral.

The caliche ore is delivered in cars of 30 to 35 tons capacity and is dumped by a revolving car dumper into the crushers (Fig 2). It varies in size from small fragments up to pieces of 2 or 3 tons. Crushing is done in three stages and reduces the ore to about 10 pct plus $\frac{1}{2}$ -in. Before the treatment process, it is screened on 20-mesh screens. About 20 pct of the total caliche to the plant is removed as fines for treatment in a filter plant and 80 pct of the ore remains as coarser material for vat leaching.

In the filter plant—of the Moore leaf type—the fines are mixed, 2 tons of fines to 1 cu meter of hot mother liquor to make a pulp of 60°C

and 1.8 density. The pulp is then ready for filtering. When cakes 1 to 1½ in. thick have been formed, the filter baskets, each having a capacity of 25 tons of cake, are transferred to a brine-wash tank for a displacement wash. Water cannot be used because of serious pitting of the cakes and, therefore, poor washing. The final washed filter cakes contain 3 to 4 pct nitrate (mostly due to the nitrate content of the brine used for washing) and are discharged into water and pumped to waste.

The coarse caliche is delivered into large concrete vats (of 7500 tons capacity in the Maria Elena plant and 12,000 metric tons capacity at Pedro de Valdivia) for leaching. There are 10 of these vats in each plant, to provide time for loading, unloading, the four-stage leaching cycle, washing and draining.

The leaching cycle consists of downward percolation of solutions, adding mother liquor to the vat in the fourth leaching stage and advancing the solution through vats in third, second and first-stage leaching to produce a strong solution. The total time of contact of the caliche with the leach solution is about 40 hr. In contrast to the Shanks process, the leaching temperature is around 40°C and the nitrate pickup from mother liquor to strong solution is from an initial 330 to a final 450 grams per liter. Space here does not permit a discussion of the influence of other salts in the caliche on the leaching and crystallizing process, except to say that temperature has little influence on the solubility of sodium chloride and sodium sulphate, so that when a strong saturated nitrate solution is cooled, sodium nitrate is precipitated, leaving practically all other salts in solution.

After leaching with mother liquor, the residue is washed with a series of graduated washes and finally with water. Extra water is always added to produce the brine wash for use in the filter plant. The vat residue, containing 1.0 to 1.5 pct nitrate, is then unloaded with 5-ton clamshell grab buckets and placed in 16-ton dump cars, which haul it to waste.

The strong solution from the vat leaching and the filter-plant leaching is combined and pumped to the crystallizing plant, which consists of a series of 20 shell and tube tanks, each containing 600 vertical tubes 3 in. in diameter and 16 ft long, and the nitrate solutions flow from one tank to another with gradual cooling from 40° to 10°C. The solution to be cooled is caused to circulate rapidly through the inside of the vertical tubes. The cooling medium is on the outside of the tubes. The first 14 tanks of the series of 20 tanks are used as recuperators—where the cooling medium is the 10°C countercurrent cooling mother liquor. The last six tanks are used as refrigerators and the cooling medium is liquid ammonia. Five 300-ton (ice-rating) York ammonia compressors service these six refrigerators.

Crystallized nitrate sludge from the crystallizers is delivered to a

battery of 24 centrifuges for dewatering. The product is pure white, about 48-mesh in crystal size; it is of 95 to 96 pct purity and contains 3.0 to 3.5 pct moisture.

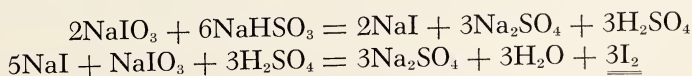
While mother liquor from the crystallizing plant emerges at 35°C, leaching temperatures throughout the plant are at 40°C. The extra heat required to heat the mother liquor as well as the caliche, and to provide for heat losses from the large open vats, is obtained as waste heat from the diesel power plant.

Of the total heat content of the fuel oil used in the 25,000-hp Maria Elena and 33,000-hp Pedro de Valdivia power plants, about 33 pct is converted to electrical energy. A large part of the remaining heat goes into the diesel cooling-water system and exhaust gases and finally is delivered to the nitrate solutions through a system of heat interchangers. In all, about 80 pct of the total heat content of the fuel oil is recovered either as electrical energy or as heat for the leach solutions. Even the ammonia condensers are cooled with leach solutions to recover the heat removed in the crystallizing plant.

In order to present to the customer in a superior form the nitrate formed by the Guggenheim process, the centrifuged nitrate is granulated. The granulation process consists in melting the centrifuged nitrate in suitable oil-fired furnaces and spraying the melt at 340°C into a large chamber. The liquid droplets, in their passage through the air, cool below the freezing point and are collected as pearl-like pellets of $\frac{1}{23}$ to $\frac{1}{8}$ -in. diameter on a belt conveyor underneath the spray chamber, and then are conveyed to coolers and finally to a storage bin for bagging or bulk shipment. The nitrate so produced has a purity of about 98.5 pct and contains small amounts of sodium chloride, sodium sulphate, borax, potassium, perchlorate and iodine (as iodate) and other salts essential for the development of plant life.

Extraction of Iodine

Iodine as an iodate dissolves in the nitrate leach solutions and builds up to concentrations of from 5 to 10 grams per liter. By the addition of sodium bisulphite (a local product made from sulphur dioxide and soda ash) the iodate is reduced to iodide. Then exactly one fifth more of the original solution containing iodate is added and solid iodine is formed, which settles to the bottom of the reaction tanks:



The spent liquor is returned to the nitrate plant and the iodine sludge is drawn off, filtered, pressed into "cheese cake" and retorted, delivering a crude product consisting of blue-black, lustrous crystals of about 99.4 pct purity. This product usually is sublimed by purchasers

for delivery to consumers. The iodine for export is packed in small wooden kegs of 70-kg capacity.

Solar Evaporation

The mother liquor used for sodium nitrate leaching is normally highly concentrated with such elements as potassium, magnesium and the borates, sulphates and chlorides present in caliche ore, with the result that these values are not dissolved from the ore and thus for many years have been discharged to waste in the plant tailings. By adding an increased volume of water wash at the end of the normal leaching cycle, these water-soluble components, however, can be readily extracted in the form of a dilute brine.

Present indications are that by the solar evaporation of these brines in suitable ponds exposed to the desert sun, substantial tonnages of potassium nitrate, additional sodium nitrate and iodine, as well as sodium sulphate, boric acid and magnesium salts may be recovered profitably.

Experimental development of such a supplementary leaching and solar-evaporation process is now well past the pilot-plant stage and the production of these additional caliche by-products may prove a very important commercial development in the near future.

Political and Commercial Control

Effective July 1, 1933, there was created by law the Chilean Nitrate and Iodine Sales Corporation. This organization, with five Fiscal Directors and five Industrial Directors and a President who by law must be Chilean, controls the commerce of nitrate and iodine. The producing industry is controlled by three large companies: The Lautaro Nitrate Co., Limited, the Compania Salitrera de Tarapaca y Antofagasta, and the Compania Salitrera Anglo-Chilena, which represent 90 pct of the entire industry. The remaining 10 pct is in the hands of small independent producers. The Lautaro and Anglo-Chilena companies, representing more than 60 pct of the industry, are owned by American and British capital under American control—the Guggenheims—whereas the Compania Salitrera de Tarapaca y Antofagasta represents British, German, American and Chilean capital with a predominating Chilean influence. The independents are principally Chilean, Spanish, Yugoslav, and French. The production of Chilean nitrate since 1931 has been as shown on Fig 3.

Specifications, Marketing, and Uses

Chilean nitrate, in accordance with the specifications laid down by the Sales Corporation, must contain a minimum of 95.5 pct sodium nitrate and a maximum of 2 pct moisture, 1.5 pct sodium chloride, 0.75

pct potassium chloride, and 0.5 pct borax. Chilean nitrate shipped to markets contains from 16.0 to 16.2 pct nitrogen and in addition contains the principal vital rare elements magnesium, iodine, boron, calcium, potassium, sodium, lithium, and strontium, which are so desirable for the proper development of plant life.

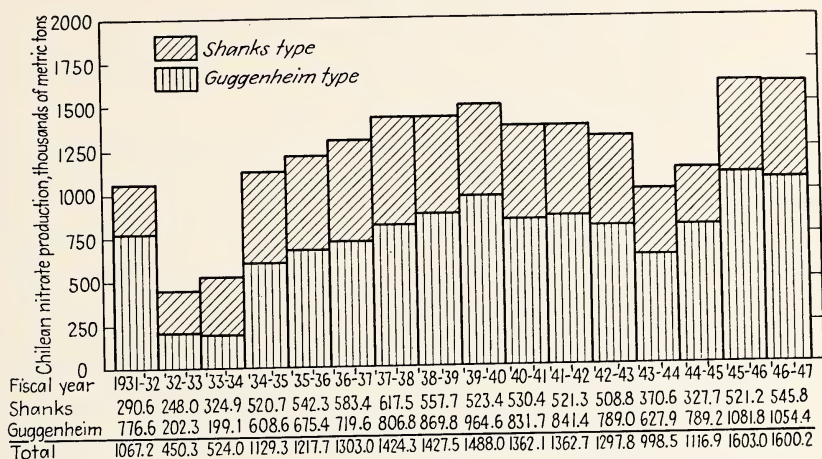


FIG 3—PRODUCTION OF CHILEAN NITRATE.

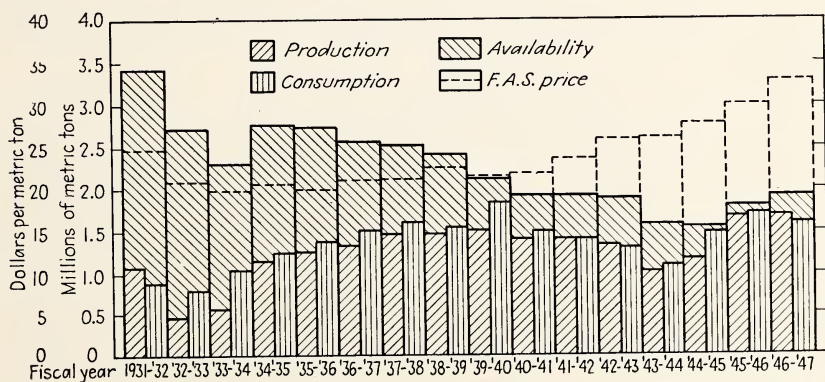


FIG 4—AVAILABILITY, PRODUCTION AND CONSUMPTION OF CHILEAN NITRATE.

Chilean nitrate is sold all over the world, the principal consumers being the United States, Egypt, Spain, Germany, France, Holland, Belgium, Sweden, Denmark, Japan, Italy, Czechoslovakia, the Baltic States, Peru, and the Argentine. Shipments are made from Chile by steamer to the principal ports of consuming countries and are distributed to dealers and consumers. The principal uses of sodium nitrate are as fertilizer and in the manufacture of chemicals and explosives.

COKE BY-PRODUCT NITROGEN

Historical Development

Second in the historical development of our present nitrogen industry—and second only to atmospheric nitrogen in potential supply—is the recovery of the nitrogen present in combined form in coal, shale and similar organic matter. The earth's coal deposits, estimated at nearly 3500 billion metric tons, contain some 40 billion tons of pure nitrogen and some 190 billion tons of hydrogen, which are released with the destructive distillation of coal to form coke.

While the distillation of coal, primarily to form metallurgical coke and to a lesser extent to produce illuminating gas, has been practiced since the latter part of the eighteenth century, the commercial recovery of nitrogen from coal in the form of ammonia gas did not begin until 100 years later. With the gradual discarding of the old beehive coke ovens—whose structure made it impossible to recover coal by-products—and the introduction of the modern by-product coke oven beginning about 1900, the coke and the gas industry became valuable contributors to the world's supply of nitrogen. With the increase in production of coke required to satisfy the expanding needs of the iron and steel industry—together with the increased production of commercial gas for illumination and heating—by-product nitrogen from coke and gas plants rapidly increased in commercial importance and took its place next to Chilean nitrate as a second important source of the world's nitrogen.

Recovery of By-product Nitrogen

In the distillation of coal, the nitrogen values are distributed between the coke, the tar, and the gaseous components. In the gaseous fraction, nitrogen is present in combination with hydrogen in the form of ammonia, which may be absorbed in water to yield aqua-ammonia or in sulphuric acid to form ammonium sulphate.

At the present time, the ammonia forms one of the most profitable by-products produced in coke and gas plants and in many cases the yield from sales of ammonia liquor or ammonium sulphate is essential to the financial stability of the coke-gas companies.

Prewar production of by-product sulphate in the United States ranged from 339,000 short tons in 1933 to 718,000 tons in 1940, with an average of 529,000 tons, according to the Bureau of Mines. Production for 1947 was reported as 820,520 tons, the increase due principally to the increased demands of the steel industry for coke.

By far the greatest portion of nitrogen recovered in the form of ammonia from coal distillation finds its outlet in commerce in the form of by-product ammonium sulphate. While the use of ammonia solu-

tions in agriculture is rapidly increasing, most of this ammonia is obtained from the atmospheric-nitrogen plants. These plants are now supplying ammonia for the production of synthetic ammonium sulphate as well and production of synthetic ammonium sulphate reached 215,000 tons in 1947.

ATMOSPHERIC NITROGEN

Nitrogen Fixation Processes

Most recent in historical development, and of major commercial importance today as a source of nitrogen and its compounds, is the earth's atmosphere, which consists principally of a mixture of two gases, nitrogen and oxygen, combined in the ratio of 4 to 1, respectively. Air contains slightly more than 78 pct of pure nitrogen gas, and the air over each acre of the earth's surface holds a potential supply of some 34,500 tons of nitrogen.

Unfortunately, free nitrogen gas is of little value to mankind, plant or animal life, and for commercial purposes it must be combined or "fixed" with other elements. The problem of nitrogen fixation on a commercial basis was first solved in Norway about 1900, with the development of the arc process, in which air passed rapidly through a zone of very high temperature produced in an electric arc furnace. Under these conditions, the principal components of the air—nitrogen and oxygen—combine to form oxides of nitrogen, which can be absorbed in water to form a dilute nitric acid.

About 1904, it was found that nitrogen from the air could also be made to combine with finely powdered calcium carbide heated to 1000°C to form calcium cyanamid—an important agricultural chemical. This was known as the Cyanamid process.

The latest and most important commercial process of nitrogen fixation is the production of synthetic ammonia; i.e., the direct formation of ammonia by passing a mixture of nitrogen and hydrogen gas over a catalyst at high temperature. The product so formed is a mixture of ammonia and unreacted nitrogen and hydrogen, from which the ammonia is removed by absorption or refrigeration. The other gases are returned to the process for further use in formation of ammonia. There are a number of variations of this direct process; among others, the Haber-Bosche, the Claude, the Fauser, and the Casale.

Ammonia by Direct Synthesis

For direct synthesis, a pure mixture of 75 pct hydrogen and 25 pct nitrogen is required. The production of the hydrogen is the most expensive phase of the process. The various direct synthesis processes in current use differ chiefly in the method by which the required hydrogen is obtained.

Nitrogen required for the synthesis of ammonia is quite readily obtained by: (1) the fractional distillation of liquefied air, which generally is employed where cheap power is available or where solid or gaseous fuels are not readily obtainable at low price, or (2) by the combustion of gas of high nitrogen content.

The production of the three volumes of hydrogen is considerably more complicated and expensive. The processes principally used are: (1) the electrolytic decomposition of water, giving oxygen as a by-product, which requires from 5000 to 6000 kw-hr of power per cubic meter of hydrogen, and thus requires low-cost electricity; (2) the treatment of water gas with steam, transforming the water and carbon monoxide into hydrogen and carbon dioxide; (3) the separation of hydrogen from coke-oven gas, natural gas or certain refinery gases. Natural gas was the source of hydrogen for most of the Government-owned synthetic plants constructed during World War II, which reportedly gave the lowest costs ever realized in making ammonia.

With the exception of the cyanamid process, all atmospheric nitrogen plants produce ammonia as their primary product. This may be compressed and marketed as anhydrous ammonia, absorbed in water to form ammonia solutions of varying strength, or oxidized to form nitric acid. Synthetic sodium nitrate is produced by the reaction of this nitric acid on soda ash. Passed into sulphuric acid, ammonia reacts to form synthetic ammonium sulphate. Absorbed in phosphoric acid, mono-ammonium phosphate is produced, and by the neutralization of ammonia with nitric acid, ammonium nitrate is formed. Nitrogen and hydrogen in the form of ammonia are thus the parents of the majority of our commercially important "synthetic nitrates."

Development of American Industry

The first attempt to establish an atmospheric-nitrogen industry in the United States was made about 1902, using the arc process, but no commercially successful synthetic ammonia plant was established here until a modified Haber-Bosch plant was installed at Syracuse, New York, by the Atmospheric Nitrogen Corporation in 1921. This was followed by installations made by Mathieson Chemical Corporation at Niagara Falls, New York; Midland Ammonia Co., Midland, Michigan; Dow Great Western Division, Pittsburg, California; and Pennsylvania Salt Manufacturing Co. at Wyandotte, Michigan. In 1926 these installations were supplemented by the addition of the Du Pont plant at Belle West, Virginia, and in 1928 by the Solvay Process Co. plant at Hopewell, Virginia. Other installations soon followed, among which were an additional Du Pont plant at Niagara Falls; Hercules Powder and Shell Chemical plants in California and the Tennessee Valley Authority installation at Muscle Shoals, Alabama.

When it became apparent that the United States would be drawn into a second European conflict, plans were immediately drawn up for the erection, with Government funds, of 10 additional synthetic-ammonia plants having a combined capacity variously rated at 650,000 to 875,000 tons of nitrogen per year. In locating these plants, first consideration was given to areas reasonably safe from enemy bombing attacks, as consistent as possible with proper facilities for the raw materials, labor, utilities and supplies. Of the 10 plants financed by the United States Government, title to eight plants was retained by the Army (Ordnance), one was transferred to the TVA (Muscle Shoals) and another to the Defense Plant Corporation (Lake Charles).

The 10 synthetic-ammonia plants erected by the Government as a defense measure, together with their potential annual capacities, are listed in Table 1.

TABLE 1—*Synthetic-ammonia Plants, World War II Period*

Plant Name	Location	Sponsor ^a	Ultimate Annual Nitrogen Capacity, Tons
Morgantown.....	Morgantown, W. Va.	Ord	71,000
Ohio River.....	West Henderson, Ky.	Ord	61,200
Missouri.....	Louisiana, Mo.	Ord	56,600
Dixie.....	Sterlington, La.	Ord	56,900
Buckeye.....	South Point, Ohio	Ord	187,000
Jayhawk.....	Baxter Springs, Kan.	Ord	128,200
Ozark.....	El Dorado, Ark.	Ord	131,200
Cactus.....	Sunray, Tex.	Ord	56,900
Lake Charles.....	Lake Charles, La.	DPC	56,900
Muscle Shoals.....	Muscle Shoals, Ala.	TVA	56,900
Total.....	862,800

^a Ord, Army Ordnance; DPC, Defense Plant Corporation; TVA, Tennessee Valley Authority.

With the conclusion of major hostilities in 1945, the great military demand for nitrogen for munitions suddenly ceased; several of the Government-owned synthetic-nitrate plants were closed and the majority were offered for sale or lease by the War Assets Administration. At first agriculture and industry were unable to absorb a post-war nitrogen output that was about double prewar consumption, and production took a downward trend toward domestic peacetime levels. Demand from devastated and famine-threatened European countries and the recognition of a great world shortage of nitrogen soon reversed this trend; the closed Government plants have now been reactivated and those offered for sale or lease are now operating at full

capacity in the hands of private owners. Salient statistics covering postwar production of nitrogen compounds in the United States are given in Table 2.

TABLE 2—*Nitrogen Compounds Produced in the United States, 1944–1946^a*
SHORT TONS, NH_3 EQUIVALENT

Calendar Year.....	1944	1945	1946
Synthetic plants (anhydrous) ^b	543,651	548,655	725,537
By-product aqua ammonia.....	31,665	27,607	24,991
By-product ammonium sulphate.....	204,561	191,073	160,938
Total.....	779,877	767,335	911,466

^a From Minerals Yearbook, Bureau of Mines, for 1946.

^b Exclusive of Government-owned plants.

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CHAPTER 33

PHOSPHATE ROCK

BY CHESTER A. FULTON*

APATITE, the most abundant crystalline phosphate mineral, is found in igneous rocks and probably is the primary origin of all other phosphates, whether mineral or organic. Its chemical formula may be expressed as $\text{Ca}_5(\text{Cl},\text{F})(\text{PO}_4)_3$. The chlorine may be replaced almost entirely by the fluorine. It is found in large or small hexagonal prisms, usually of a vitreous luster and a green or red color, but also violet, white, or yellow. It is found largely as an accessory mineral in granitoid rocks. Its hardness is 4.5 to 5 and its specific gravity is about 3.2.

There are many other phosphate minerals—for instance, amblygonite, autonite, collophane, lazulite, monazite, pyromorphite, torbenite, triphylite, turquoise, vivanite, wavellite—with base elements of calcium, magnesium, iron, aluminum, manganese, lead, cerium, lanthanum, lithium, or several of these in combination and with various amounts of water of crystallization. However, these phosphate minerals have but little value save as specimens for mineral collections, the exception perhaps being turquoise.

While large deposits of igneous apatite are mined today for the production of fertilizers and chemicals, more than 90 pct of the world phosphate production is derived from *secondary* apatites, called phosphorites. These calcium (and magnesium, aluminum, and iron) phosphates have been formed in the alteration of sediments by solutions containing phosphoric acid. Such solutions have come from the weathering or leaching of igneous rocks containing apatite, bone deposits of prehistoric animals and marine life, or guano deposits (excreta of birds). These phosphorites are mostly alterations of phosphatic limestones that took place slowly over many years. Whether it is apatite or phosphorite that is being produced, it is known in the trade as “phosphate rock.”

The sedimentary phosphate deposits are of marine origin. Some, as laid down, were rich in phosphate or have become so by subsequent subaqueous action and have not been further enriched since emergence from the sea. Some were originally phosphatic limestones or marls from which calcium carbonate was dissolved away by waters containing carbon dioxide, in which calcium carbonate is much more soluble than

* Consulting Mining Engineer, New York, N. Y.

calcium phosphate, leaving a residue correspondingly enriched in the latter. This enrichment may have been increased by the interchange of dissolved phosphate ions in the waters for carbonate ions of the rock mineral. Some deposits may be due to the transportation by flowing water of phosphatic residues from the weathering of surface rocks and their re-deposition with other debris in shallow coastal waters. Yet other deposits may have been formed on beaches as the result of the disintegration of phosphate-bearing cliffs and the sorting action of waves. More than one of these agencies may have contributed to the formation of any deposit, now sufficiently high in calcium phosphate to be an economical source thereof.

USES OF PHOSPHATE

Without phosphates, plant life cannot survive. With insufficient phosphates, plant life cannot thrive. Before the time of man, the phosphate in all vegetation traveled a cycle, it went from the soil into the plant and when the plant, or its parts, decayed and died, the phosphate returned to the soil from whence it came. Where soil was deficient in phosphate, little vegetation grew. Where there was soil rich in phosphate, dense forests and undergrowth flourished, other necessary conditions for plant life prevailing.

When, in the process of agricultural evolution, the products of the soil were removed to cities and other areas far from the land where they were grown, impoverishment of the phosphate content of the soil was a natural consequence and, in order to maintain fertility, it became necessary to add phosphate to the land. It was not until near the end of the eighteenth century that some farmers began to use ground bones, or bone meal, as an application to the soil to replace the phosphate that was removed by harvested crops shipped to other places.

About 1840, Liebig suggested that bones be treated with sulphuric acid to render the phosphate in them more soluble and more quickly available to the crop.⁶ Soon, however, the supply of bones became inadequate for the demand. In 1842, John Bennet Lawes, an English farmer, patented a process for acidulating phosphatic nodules, or coprolites, a phosphorite of which there were then known deposits in England as well as in Spain. Lawes called his product "superphosphate."⁶ This is the term used today for the product resulting from the acidulation of phosphate rock. Superphosphate is the largest ingredient in mixed commercial fertilizers in the United States, where the custom is to sell "complete" fertilizers containing nitrogen (N), phosphoric acid (P_2O_5), and potash (K_2O). A 5-10-5 fertilizer under any brand name must contain these percentages of N, P_2O_5 , and K_2O in available form.

Phosphate rock is sold usually by the long ton of 2240 lb, or the metric ton of 2204.6 lb. Its price per ton is based upon its grade in tricalcium phosphate $Ca_3(PO_4)_2$, commonly known in the trade as bone

phosphate of lime, or BPL. Grades of rock sold vary greatly, running from about 50 pct up to 85 pct BPL.

In normal times about 90 pct of the phosphate rock mined is consumed by the manufacturers of superphosphate and other phosphate compounds for fertilizers or, after fine grinding, for direct application to the soil. In other words, phosphate rock is mined principally for the benefit of agriculture. The remainder of the rock mined is used for making elemental phosphorus, from which are made many pure phosphate chemicals, such as disodium phosphate used in the silk industry, monocalcium phosphate in baking powders, as water softeners, rust-proofing compounds, and in the manufacture of glass. Phosphates are used also in ceramic products, beverages, dental cements, photography, fireproofing compounds, sugar refining, and in fermentation processes.¹⁵ During World War II, an extraordinary amount of elemental phosphorus was produced for incendiary bombs.

MANUFACTURE OF PRODUCTS

Superphosphate is manufactured by acidulating finely ground phosphate rock with sulphuric acid. The result is a conversion of about 80 pct of the tricalcium phosphate $\text{Ca}_3(\text{PO}_4)_2$, to monocalcium phosphate $\text{CaH}_4(\text{PO}_4)_2$, and about 15 to 17 pct to dicalcium phosphate $\text{Ca}_2\text{H}_2(\text{PO}_4)_2$, the remainder of the tricalcium phosphate being unchanged or having changed to insoluble iron and aluminum phosphates.

Monocalcium phosphate is soluble in water, dicalcium phosphate is soluble in ammonium citrate, and together they are considered "available" phosphates for plant food in the United States and Canada. The calcium thus removed from the tricalcium phosphate is still in the superphosphate but it is there as hydrated calcium sulphate (gypsum) and really dilutes the final product, superphosphate. For example, one long ton of phosphate rock, 74 pct BPL, containing 33.9 pct P_2O_5 , will make almost two short tons of superphosphate containing only 20 pct P_2O_5 . Therefore, the superphosphate plants must be close to the fertilizer-consuming centers, to avoid rail haulage.

In the larger superphosphate plants about one half of the fluorine in the phosphate rock is recovered and used in the manufacture of fluosilicates, valuable for insecticides, concrete hardeners, and other uses.

Early in the twentieth century, the manufacture of triple superphosphate started and it has grown in tonnage. Triple-super contains from 45 to 48 pct available P_2O_5 , most of it water-soluble. The process uses sulphuric acid in sufficient quantity and strength to convert nearly all the calcium in the rock to calcium sulphate and the P_2O_5 to orthophosphoric acid H_3PO_4 . Additional phosphate rock is then acidulated with this phosphoric acid, so that practically all of its tricalcium phosphate is converted to monocalcium phosphate and there is no dilution by cal-

cium sulphate, hence the high P_2O_5 content of triple-super. In many places, this makes possible a triple-super plant near the mines, providing sulphuric acid is available there at a sufficiently low cost.

The blast furnace and the electric furnace have been used in the production of elemental phosphorus, phosphorus pentoxide P_2O_5 and orthophosphoric acid H_3PO_4 . However, the blast furnace appears to have given way to the electric furnace where power is cheap.

The production of phosphorus and orthophosphoric acid by the electric furnace requires very cheap electrical energy—not much over 2 mils per kilowatt-hour. If this acid is to be used in making triple-super, it can compete with the sulphuric acid process only under especially favorable conditions of location. An advantage claimed for the electric-furnace process over the wet process is that a much lower grade of phosphate rock can be used because its impurities (iron, alumina, silica) replace a certain amount of the fluxing material in the furnace charge to make a fusible slag and free the phosphorus. Another advantage is that elemental phosphorus is a 100 pct concentrate and one short ton of it contains as much phosphorus as 6 long tons of the average grade of phosphate rock. Therefore, it can be shipped in tank cars for comparatively long hauls to consuming centers at competitive freight rates. That would be true only if the phosphorus were produced at places where power cost is about 2 mils per kilowatt-hour and it does not take into account the cost of the limestone or phosphate rock needed to make triple-super at such a plant in the consuming center.

The Tennessee Valley Authority has made much progress in developing the electric furnace for the production of elemental phosphorus at Muscle Shoals but there power is very cheap.⁶ The TVA has produced calcium metaphosphate $Ca(PO_3)_2$ from hot P_2O_5 gas passed through a bed of phosphate rock. This metaphosphate, which is relatively new as a fertilizer material, contains about 64 pct of P_2O_5 , of which all but about 2 pct is available as plant food.⁶

Other phosphate fertilizer products, such as Rhenania, Bernard (Germany), Kotka (Finland), Supertomasyna (Poland), Limphos (Great Britain), Orafosfat (Norway), ammonium phosphate, and other concentrated fertilizers are sold under various trade names.⁶

PHOSPHATE DEPOSITS

Phosphate-rock deposits are found in many parts of the world. Probably there are very few countries where phosphate deposits of some kind have not been found. Many of them have been exhausted and abandoned during the past hundred years because of meager reserves, low grade, or too costly mining, when cheaper phosphate rock could be obtained from the large mines of low-cost production. Only the phosphate-rock fields, or areas, that have been steady suppliers of the world during the past 20 years will be described.

United States

There are four producing phosphate-rock fields in the United States, known as Florida Pebble, Florida Hard Rock, Tennessee, and Western (Fig 1).

FLORIDA PEBBLE FIELD

The Florida pebble field,⁵ accounting for about 70 pct of the total American production, is in the western part of Polk County and parts of other counties adjacent thereto. It is about 50 miles by rail from Tampa and Port Tampa, on the Gulf Coast, where special tidewater terminals are maintained by two large railroad systems for loading phosphate rock for seaborne shipments.

The pebble phosphate is found in alluvial deposits of Pliocene age mixed with sand and clay. This bed is called locally the "matrix." It varies in thickness from a few feet to about 25 ft and underlies an overburden of about twice its thickness, though this varies considerably. The overburden is composed of sand and clay, and in places a bit of "hard-pan" in thin beds. The phosphate pebble in the matrix varies in size from pebbles of about 2 in. in diameter down to micron sizes, and generally the finer the pebble, the higher its grade in BPL.

This pebble came from the erosion of the Hawthorne marl of Miocene age. The detritus from this erosion apparently settled out in basins or depressions underwater together with the sand and clay from other near-by formations, forming what is today called the matrix, containing from 10 to 35 pct phosphate pebble. The phosphate rock is now covered with a barren overburden.

Seven mining companies are operating in the field, with a total of about 15 mines, each with its large dragline and its own ore-dressing plant, locally called a "washer," from the early days when only the coarse pebble was recovered by screening.

At most of the mines, the overburden, from 10 to 50 ft thick, and the matrix below it, from zero to 35 ft thick, containing the phosphate pebble, are now excavated by large draglines. These excavators usually are of the "walker" type, electrically driven, with booms varying from 150 to over 200 ft in length and carrying buckets that vary in capacity from 10 to more than 20 cu yd. These draglines are capable of removing overburden at the rate of from 600 up to about 1500 cu yd per hour and excavating the matrix at the rate of from 300 to 1000 cu yd per hour.

The dragline removes the overburden and dumps it into a mined-out area at the side. It then lifts the matrix and dumps it into an improvised small sump in the overburden on undisturbed land within reach. Here it is mixed with water. From this sump, a large, portable electric pump moves the slurry through a steel pipe line (casing type) to the washer. A

hydraulic giant (called a "gun") supplies the water to the sump and also helps to make a good slurry of the matrix. As the mining operations get farther and farther away from the washer, booster pumps are put into this "rock line" to maintain a steady flow to the washer.

While the mines usually operate three shifts daily of 8 hr each, the average time of actual production is nearer 20 hr daily, owing to moving of equipment as the mining progresses, installing piping and power lines on the move, installing booster pumps in the "rock line" through which the slurry is pumped, electric-power failures caused by storms, and other temporary shutdowns.

However, with a matrix containing 25 pct pebble, and 85 pct recovery at the washer, mining at the rate of 350 yd of matrix hourly, a day's production of phosphate rock from the washer will amount to about 1500 long tons (dry basis.) If the matrix contains 35 pct pebble, production will be 2100 tons, while a 10 pct matrix will yield only 600 tons. Mining matrix at a greater rate than 350 cu yd per hour, by using larger drag-lines, will increase production proportionately. It is plain that the cost of producing pebble phosphate depends very much on the yardage (overburden and matrix) that must be handled per ton of phosphate pebble produced.

All phosphate lands in the pebble field are thoroughly prospected and each company knows closely the recoverable tonnage per acre and the yards per ton of both overburden and matrix. The prospecting is done by sinking $4\frac{1}{2}$ -in. auger holes (one hole to each $2\frac{1}{2}$ acres) through overburden and matrix to the bedrock below. The core from the matrix is treated in a miniature washer for recovery of the plus 20-mesh screened and sized rock. Flotation tests are made in the laboratory to determine the recoverable minus 20-mesh pebble. All data are plotted on maps, and from such maps the washer sites are easily located.

On arrival at the washer plant, the slurry is passed through trommels to remove debris and large clay-balls.¹⁴ The disintegration of the smaller clay-balls is accomplished by log washers and Hardinge mills. The clay slime (including the unrecoverable phosphate of the micron sizes), is removed by various types of deslimers, including Dorr, hydro-separators, deslimers and Allen tanks. Plus 5-mesh pebble is recovered by vibrating screens; minus 5-mesh, plus about 20-mesh, is recovered by screens or Fahrenwald sizers, from the first two or three compartments of which the pebble is free of silica sand. The maximum size of the silica sand varies between 18 and 20-mesh. The pebble from the remaining compartments is diluted with silica sand of about the same size and this is the feed to the agglomeration tables or the flotation cells, or both.¹⁴ Spirals may replace tables.

The process of floating the phosphate pebble varies considerably at different plants, owing to the percentage of the minus 20-mesh phos-

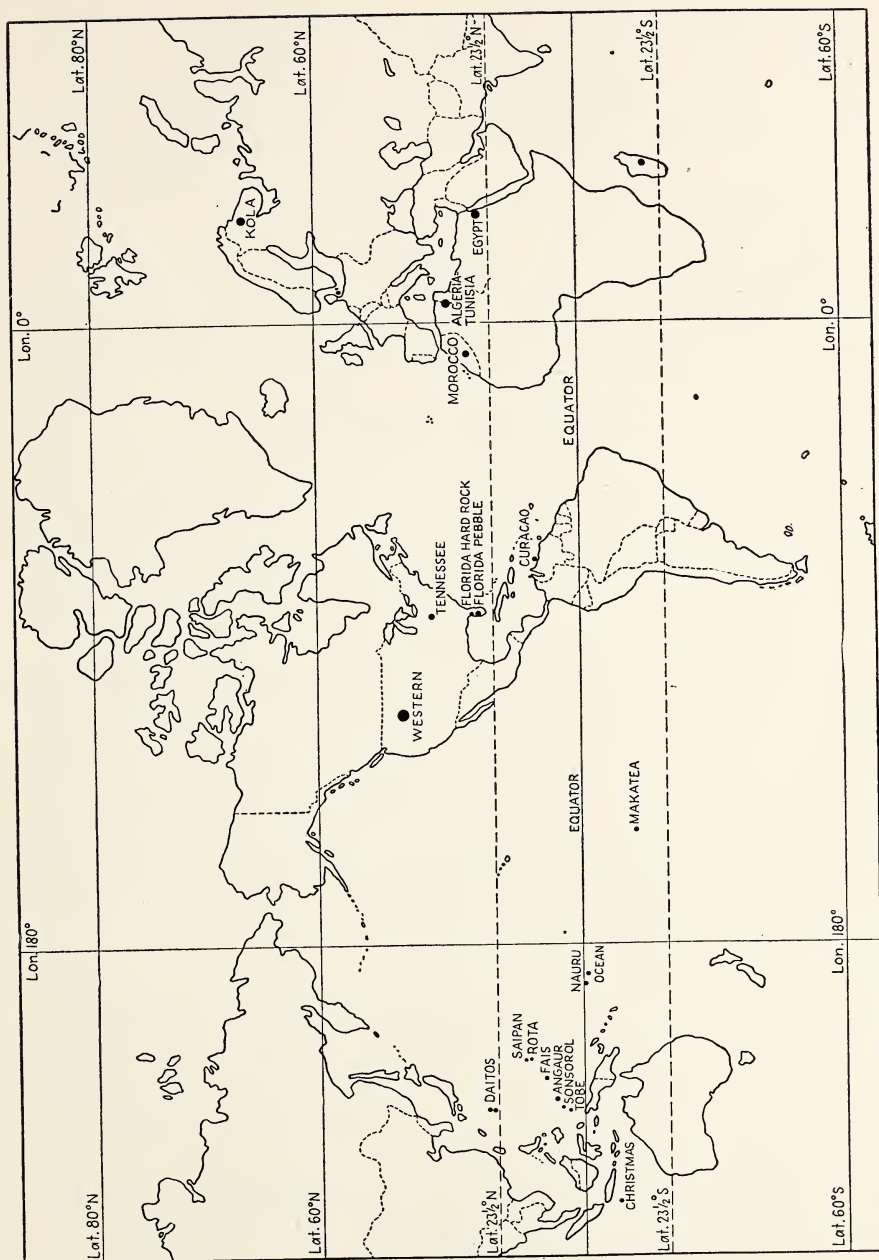


FIG 1—WORLD MAP SHOWING LOCATIONS OF IMPORTANT PHOSPHATE-ROCK DEPOSITS.

phate pebble in the matrix being treated. This varies from about 20 pct of the total phosphate in the lower grade (66 to 68 pct BPL) deposits up to 85 pct in the higher grade deposits, though there are high-grade deposits containing as little as 50 pct minus 20-mesh pebble. The flotation reagents used are caustic soda, a fatty or resinous acid, and fuel oil. The pH of the pulp, which is normally about 7, must be raised to between 8 and 9.¹⁴

The sized products in the washer bins are known as "wet rock" and are transported by rail to the central drying plants of the several operating companies. As a rule, very little storage capacity is provided at the washers, as the railroads spot enough empty wet-rock cars every day for the following 24 hr of production. These cars are bottom-dump gondolas. The haul from the washers to the central drying plants varies from about one mile up to 25 miles. Wet-rock shipments contain from 10 to 20 pct moisture.

Shortly after arrival of the wet rock at the central drying plant, the grade of rock in each car is known from car samples of the previous day, and the cars are dumped from a trestle to storage piles beneath according to grade and size of pebble. This wet-rock storage varies from 50,000 up to 200,000 long tons, dry basis.

From the wet-rock storage, the phosphate is handled entirely mechanically until it finally reaches the dry-rock cars in which it is shipped.² In its passage through the drying plant, it is dried to between 1 and 2 pct moisture in rotary driers. These driers are fed at the fire end. They are about 7 ft in diameter by 60 ft long or larger, and are equipped with fuel-oil superheaters, atomizers, cyclones, and fans. The dry dock as it leaves the rotary drier has a temperature between 212° and 280°F. About 3 to 4 gal of Bunker C fuel oil is consumed per ton of rock dried.

Some of the drying plants also have rotary kilns similar to cement kilns, but smaller, for calcining phosphate rock at temperatures between 1500° and 1600°F. In this treatment, the moisture and the 2 to 3 pct of organic matter is driven out and the BPL grade is raised correspondingly.² Phosphate rock free of organic matter is used in making colorless phosphoric acid for the manufacture of white phosphate chemicals, used in baking powders and for weighting silk.

Belt conveyors deliver the dried or calcined rock to a storage bin divided into compartments, so that it can be classified as to grade or type and shipped out within a week or ten days.

The dry-rock storage bins usually are of reinforced concrete or steel, though some old wooden bins are still being used. They vary in capacity but most bins hold about 25,000 long tons.

For all rail shipments to interior points, boxcars are loaded by special mechanical loaders receiving their rock from flexible steel spouts in

the floor of the bin. On export shipments and those to domestic coastal ports, the bin loads directly into special dry-rock cars, hopper-bottomed and decked over on top, which are hauled to Port Tampa or to Tampa, where special facilities are maintained for loading ships. At Tampa the loading is 600 long tons per hour while at Port Tampa it is 1200 long tons per hour.²

Shipments from the Florida pebble field in 1947 amounted to 6,314,-077 long tons having an average grade of 72.98 pct BPL.⁹ This is a new record. The war and its aftermath have curtailed very much the exports of Florida pebble, which in 1930 reached over a million tons and in 1941 totaled 863,347 tons. However, domestic trade had increased from 2,416,359 tons in 1941 to 4,473,522 tons in 1946.

FLORIDA HARD-ROCK FIELD

The Florida hard-rock field is about 100 miles to the north of the pebble field. The deposits are of Pliocene age and were derived from the Hawthorne marls. They are mixtures of rather hard phosphate, in the form of fragments and boulders varying in size from one inch to masses of several tons, in a matrix of sand, clay, chert, and soft phosphate.

The principal operation in this field, accounting for almost all of its production, is that of the mine near Dunnellon, Marion County, known as the Section 12 mine, where two companies have combined their operations for economy.

At this mine, the overburden, which generally is not thick, is removed by hydraulicking. The matrix is excavated by a 3-yd dragline and hauled to the washer by skipcar. At the washer, the hard rock is concentrated by screening through grizzlies to remove waste boulders and other debris, then goes through log washers, classifiers, sizers, and tables. All of the production is high grade, from 77 or 76 pct up to 80 pct BPL.

The hard-rock phosphate is shipped from the washer to a drying plant at Fernandina, on the Atlantic coast north of Jacksonville, a railroad haul of about 150 miles. There it is dried in rotary driers and loaded directly into ocean-going vessels.

In the past 20 years, most of the production from the hard-rock field has been exported to Europe, therefore this field has been adversely affected by the difficulties of export trade since the beginning of the war. Shipments in 1947 amounted to 79,330 long tons, with an average grade of 77.81 pct BPL, of which practically all was exported.⁹ Prior to the war, Florida hard rock had reached yearly productions as high as 125,000 tons, most of which was exported to Europe.

Besides the hard rock in this field, there is now produced an appreciable tonnage of so-called "soft rock." This is generally recovered from

the mined-out hard-rock pits. It is a concentration of fines from the hard-rock mining operations. In the past, this tonnage was unimportant and found its market in the immediate vicinity for direct application to the soil. In 1947, these soft-rock shipments reached a high of 88,620 long tons, or more than the hard-rock shipments. Average grade was 44.31 pct BPL.

The total shipments from the hard-rock field have been 167,950 tons with an average grade of 60.92 pct BPL.

TENNESSEE FIELD

The Tennessee field is in the central basin of Tennessee. Three types of phosphate are recognized—brown, blue, and white. The brown phosphate represents almost all of the phosphate rock produced in Tennessee today. It consists of residual deposits derived from several formations of Ordovician age. They lie on an irregular floor of limestone and in the depressions have accumulated the less soluble phosphates. These deposits range up to as much as 50 ft in thickness in the deeper depressions.

Draglines, much smaller than those used in Florida, remove the overburden and excavate the phosphate matrix, which grades 35 to 60 pct BPL. After treatment in the washer, however, it will have been concentrated to about 60 to 72 pct BPL. It is then dried and shipped to manufacturers of superphosphate and to electric-furnace plants for production of phosphorus. Some matrix is used directly as a furnace burden.

Tennessee brown rock is rather high in the oxides of iron and aluminum, known in the trade as "I&A." It rarely runs less than 5 pct I&A and often more. I&A has a tendency to make insoluble iron and aluminum phosphates and therefore above certain limits is considered undesirable by the superphosphate manufacturer. Florida pebble is generally sold on the basis of a maximum of 3 pct I&A and usually contains much less. For this reason the sales area for Tennessee rock prior to World War II was north and west of a line drawn from Little Rock, Arkansas, through Jackson, Mississippi, Atlanta, Georgia, and thence northwestward following the Appalachian Mountains. This was true even though Tennessee rock could be laid down near this line for one dollar per ton less than pebble phosphate from Florida.

The Tennessee Valley Authority has sizable operations in Tennessee and during the fiscal year ended June 30, 1945, mined approximately 517,000 tons of phosphate matrix and processed in its Godwin washing plant at least 525,000 tons averaging 45 pct BPL.⁹ This yielded 242,000 tons of phosphate sands grading 57 pct BPL. About 67,300 tons of lump sinter and sinter fines was shipped to Muscle Shoals, Alabama. From other miners in the field, TVA purchased 121,000 tons of sinter

and washed sands. Production of elemental phosphorus during the fiscal year reached 29,800 tons, mostly for the Chemical Warfare Service.

Tennessee brown rock (including sintered matrix) in 1947 was mined by the TVA and seven private companies. Total production (including blue rock) for 1945 was 1,411,884 tons, averaging 61.84 pct BPL.⁹ The low grade was due to matrix mined for the electric furnace, which is included in the total tonnage produced.

These figures include a small tonnage of apatite from Piney River, Virginia, where there is an igneous deposit in pre-Cambrian granite gneiss consisting of a mixture of feldspar, ilmenite, and apatite. The ultimate consumption of the apatite is probably for fertilizer purposes and the ilmenite is recovered for its titanium.

WESTERN FIELD

From a point about 50 miles to the east of Salt Lake City, there is a series of deposits of phosphorites in an area running slightly west of north to a point west of Helena, for a distance of about 350 miles with a width of about 100 miles and traversing the states of Utah, Wyoming, Idaho, and Montana. This phosphatized area has a continuation in Canada near Banff.¹²

The phosphorite occurs in two sedimentary formations, one of Upper Mississippian age, which is of little importance, and the other of Permian age, in which the major deposits of this field are found in regular beds like sandstone and shale, and are of marine origin. These beds have been folded, faulted, and eroded and are found at all angles of dip from horizontal to vertical.

Prospecting, development, and mining have been carried on in the Western field for the past 20 years, starting probably in Idaho. The Anderson mine, near Garison, Montana, first came to notice in the early 1930s. In 1942, Utah came in with slightly more than one thousand tons production but did not repeat until 1946. In 1947, all four states were producing; Idaho and Utah together shipped 905,214 tons, Montana, 236,229, and Wyoming, 51,845, for a total Western field shipments of 1,193,288 long tons averaging about 70 pct BPL. This record tonnage came from the mining operations of 10 companies. Two other companies did development work but made no shipments.⁹

The future of the Western field is very promising for it should supply the agricultural phosphate needs in the western states, approximately that area lying west of a line drawn from, let us say, San Antonio, Texas, to Saint Paul, Minnesota. Today this area is not putting back into the soil the phosphates removed by cropping, not even in California (1944). The reason for this is that fertilizer phosphates that originate in the phosphate rocks from Florida or Tennessee become very high in cost in this area because of the long haul.

With cheap power to the phosphate mines in the Western field³ promised by the Bonneville Power Administration within the next few years, and the improvement in the electric-furnace process, it may be economical to produce elemental phosphorus at or near the western mines and ship it to plants in the center of western agriculture for conversion there to superphosphates. This would mean, eventually, the development of a very large phosphate-rock production in the Western field and at low costs per ton. More than half of the phosphate-rock reserves of the United States are in this field.

Production of phosphate rock in the United States in 1947 made a new record of 9,121,081 long tons, an increase over 1946 of almost two million long tons. Of this, Florida (including pebble and hard-rock fields) accounts for over a million tons; the Western field increased about 700,000 long tons; the rest of the increase came from the Tennessee field. Exports amount to 1,684,728 long tons (a record), of which 772,553 long tons came from Florida and 912,175 long tons from the Western field, shipping to Japan and Canada.

OTHER DEPOSITS IN UNITED STATES

Other phosphate deposits in the United States have been mined and at one time were relatively large and important producers, such as those in South Carolina and the river pebble deposits of Florida. Still others of minor importance have been worked at times in a small way, such as those in Kentucky and Arkansas. In the central part of Kentucky brown phosphate deposits have been found in Fayette, Woodford, Scott, Jessamine, Franklin, and Clark Counties. Some phosphate was produced there prior to 1927.¹² In the northern part of Arkansas, in Stone, Izard, Searcy, Marion, Baxter, Newton, and Independence Counties, phosphates occur in late Ordovician shales as original sedimentary deposits. Some mining was carried on between 1900 and 1912.¹²

French North Africa

In the three countries, Morocco, Algeria, and Tunisia, forming the northwestern part of Africa, with a coast line of 600 miles on the Atlantic Ocean and 1250 miles along the Mediterranean, are two phosphate fields of great importance. One is entirely within the borders of Morocco, a French protectorate, and the other is on either side of the borderline between Algeria (politically part of France) and Tunisia, a French protectorate.

MOROCCO

The deposits in Morocco are in sediments between the Atlas Mountains to the east and the Atlantic coast to the west, traversing an area in the rolling plain for a distance of about 200 miles. These sediments are of the Eocene period and are composed of shales, limestones, and

sandstones, usually only moderately folded. The phosphate being mined is an altered limestone, probably of marine origin, in the form of gently dipping beds 6 to 10 ft thick in these sediments. There are other parallel phosphorite beds, which are less attractive from the mining viewpoint.

The largest producing mine is at Kourigha, where the deposit has been opened up by three main adits on the downslope of the bed, approximately 5 to 10 pct grade, traversing the bed to the underground-water level, a distance of 3000 to 8000 ft as measured along the incline. A room-and-pillar method of mining is used. The thickness of the bed of phosphorite is about 10 ft. The pillars are mined later by retreating methods similar to longwall mining. It was stated to the author (on a visit to the mine in 1938) that the deposit was so extensive it would be many years before the phosphate rock above the water level would become exhausted, and that no plans had been made for the future mining of the phosphate below water level. The phosphorite, being relatively soft, was mined with a minimum of drilling and blasting. It was loaded into small mine cars and hand-trammed to the main haulage tunnels. There the cars were attached to an endless cable and hauled out of the three main adits to the drying plant near by. At the drying plant, the large lumps were crushed and passed to trommels, where the oversize (wall rock) was removed, the remainder going to wet-rock storage bins. These bins had a capacity of about 75,000 to 100,000 metric tons. From there the phosphate rock was fed to cylindrical driers, which delivered it to the dry-rock bins.

During about four months in the summer, the rock is not passed through the driers but is spread out on the ground for sun-drying, for which there is a specially designed layout equipped with three types of diesel machines, one for taking phosphate from cars and spreading it evenly about a foot or two deep; another to rake over these beds, and a third to excavate them, loading the phosphate into cars ready for haulage about 90 miles to the port of Casablanca, on the Atlantic coast, over a one-meter-gauge electric railway. There, at a special phosphate pier, the cars are dumped mechanically and by means of an elaborate belt-conveyor system the phosphate is placed in storage bins holding about 75,000 tons. From these bins phosphate rock is loaded into ocean-going vessels at the rate of 1000 metric tons per hour.

Kourigha was the first phosphate-rock mine developed in Morocco, and came into the market about 1925. Its rock is known in the trade as "Morocco phosphate," guaranteed to grade not less than 73 pct BPL; usually it runs about 75 pct BPL. Kourigha came into production as phosphate consumption in Europe was rapidly increasing and because of its lower freight rates was supplying Europe by 1937 with more than a million tons annually through Casablanca.

The other phosphate mine in Morocco is known as the Louis Gentil.

It is about 130 miles southwest of Kourigha. Development work commenced about 1930 and shipments began in 1935. Its operation is very similar to that at Kourigha but there is only one main haulage adit. The phosphorite bed is of about the same thickness and in 1938 the same method of mining was used. The rock is hauled out of the adit by cars attached to an endless cableway, delivering them to a small crushing plant. It is hand-picked on traveling steel belts for the removal of chert and wall rock and then is delivered to storage. A belt-bucket excavator delivers the phosphate to an aerial tramway, which carries it $2\frac{1}{2}$ miles over rolling country to the drying plant at the village of Louis Gentil. The drying plant is similar to that at Kourigha, but smaller. From the dry-rock storage bins, the rock is hauled by rail about 35 miles to the port of Safi, which is on the coast about 140 miles south of Casablanca. There a similar but smaller layout for storage and boat loading is installed. Louis Gentil phosphate, known in the trade as "Safi phosphate," grades about 70 pct BPL.

The war and the occupation of Morocco by Germany affected adversely the tonnage shipments from Morocco, which dropped from 1,703,000 metric tons in 1939 to a low of 511,500 in 1941. Since then, shipments have gradually recovered, especially after 1943, to 2,234,600 metric tons in 1947. During the German occupation most of the phosphate shipped went to Germany and Italy.

ALGERIA-TUNISIA

Along the border between the Province of Algeria and the Regency of Tunisia, starting about 75 miles south of the Mediterranean, there extends a series of phosphate deposits 125 miles southward to Metlaoui. These deposits, which are found on both sides of the border, are phosphorites in sediments similar to those in Morocco, but are of lower Eocene age. With a few exceptions, all mining is underground, the beds have a small angle of dip, and are opened by means of main adits similar to those in Morocco. The mining methods are also similar. The phosphate beds vary in thickness up to about 10 ft. Some beds break into very fine fragments while others produce large fragments mixed with fines.

In Algeria, the important operation is at Djebel Kouif, about 25 miles north of Tebessa, and belongs to the Cie. des Phosphates de Constantine (known as "Constantine"). This mine has produced for many years but reserves are sufficient for only a few years more. Therefore, Constantine has developed another deposit about 60 miles south of Tebessa, called Djebel Onk, which will continue the supply of phosphate rock from this company. Transportation is over cableways and a narrow-gauge railway to Tebessa, from which the state railway takes it to the port of Bone on the Mediterranean. Production from the operations of Constantine has been generally over 500,000 tons annually.

A much smaller mine on the Algerian side is that of M'Zaita, producing a hard, lumpy phosphate, which is shipped through the port of Bougie for metallurgical demand in Europe.

On the Tunisian side of the border, the largest producer is the Cie. des Phosphates de Gafsa, which operates mines at Metlaoui and Redeyef. These mines are similar to those at Djebel Kouif. The beds vary in thickness from about 6 to 8 ft. Mining methods are similar to those used in Morocco. As these mines are in a very dry country, only about 50 miles from the sandy desert of Sahara, the mined phosphate rock is sun-dried during the entire year in a manner similar to that employed at Kourigha, Morocco. The mines are very well equipped, which accounts for their large production. The Gafsa company normally produces about 1,400,000 metric tons annually; therefore it is one of the largest producers of phosphate rock in the world.

The Gafsa company owns also the meter-gauge railway system that connects Metlaoui and Gafsa to the ports of Sfax (150 miles) and Sousse (200 miles), on the eastern coast of Tunisia, as well as with the state railways that lead to Tunis and the northern coast. At both Sfax and Sousse are well-equipped piers for loading phosphate rock into ocean-going boats.

Phosphates in Tunisia are mined also by the companies known in the industry briefly as Tunisiens, M'Dilla, Dyr, and St. Gobain.

In 1939, Algeria produced about 500,000 metric tons and Tunisia 1,188,000 tons, or a total from this field of 1,688,000 metric tons. This gradually dropped during the war to a low in 1943 of 77,000 tons from Algeria, 335,000 tons from Tunisia, or a total of only 412,000 tons. Production gradually improved in the years that followed and in 1947 Algeria produced 706,878 tons and Tunisia 1,759,236 tons; a total of 2,466,114 tons for this field. This is an increase of almost 50 pct since before World War II.⁹ Compared with other producing fields, the grades produced are lower, varying from 58 to 66 pct BPL.

EGYPTIAN DEPOSITS

Phosphate rock was first mined in Egypt in 1908 on the banks of the Nile. There are two producing companies, one at Safaga, about 280 miles southeast of Cairo and 18 miles inland from the Red Sea, operated by an English company; the other at Kosseir, to the south of Safaga, belonging to an Italian company.

The Egyptian deposits are phosphorites in Cretaceous sediments and are similar to the Algeria-Tunisian deposits.

At Safaga, the mining so far has been surface mining along the outcrop and to a relatively shallow depth, because the cost of removing overburden soon becomes uneconomic. At Kosseir, the mining is underground, by the room-and-pillar system.

In the years immediately preceding the war, most of the Egyptian production was shipped to Japan. As war interfered with such movements, production dropped from 548,000 metric tons in 1939 to 143,000 in 1940 and to a low of 112,000 tons in 1941. Since then there has been some recovery and production is fairly constant between 300,000 and 400,000 metric tons annually. Egyptian phosphate rock grades usually about 66 to 68 pct BPL and is higher in carbon dioxide than other phosphates.

RUSSIAN DEPOSITS

Phosphate production in Russia⁶ started about 1885. There are many deposits of phosphorites in European Russia, among which are those at Podolia and Bessarabia. Those at Podolia have been used for many years for the manufacture of superphosphate. From the Kostroma and Viatka phosphates, low-grade superphosphate (12 pct P_2O_5) has been made for a long time. Low-grade phosphorites at Smolensk, Kursk, Voronech, Saratoff, Simbirsk, and Voleyda have been ground finely and used for direct application to the soil.

About 1930, in the northern part of European Russia, within the Arctic Circle, a huge deposit of igneous apatite was discovered, and its development into one of the largest phosphate producers was begun by the Soviet Government. It is in the Kola Peninsula, about 100 miles by rail south of the port of Murmansk, which is on a wide river flowing to the Barents Sea. It is about 700 miles by rail north of Leningrad.

This deposit forms a mountain of apatite somewhat diluted by nephelite, aegirite, titanomagnetite and sphene (titanite). The mine has been opened by driving into the deposit a large haulage tunnel capable of taking complete trains of ore cars of outside railroad gauge. From this main tunnel, smaller tunnels totaling about 20 miles in length have been driven and equipped with electric haulage. At the town of Kirovsk, not far from the mine entrance, the Government has built a large concentrating plant, equipped with crushers and grinding mills. The major part of the mine production is treated by flotation to produce a high grade of apatite, up to 88 pct BPL. It is said that the sphene and titanomagnetite are separately recovered by flotation for the production of titanium. The part of the phosphate production that is not concentrated is shipped direct to metallurgical plants. The annual output of crude and concentrate is said to be more than 2,000,000 metric tons.

Apatite is not always competitive with phosphorites on an equal basis because of its lack of porosity. It is a crystalline mineral and therefore solid, whereas phosphorites are very finely porous, even appearing to be dry when actually containing up to 5 pct moisture held in the very fine pores. When apatite is treated with sulphuric acid, it

is attacked only on the surface of the grains, whereas the phosphorite particles are attacked also within their pores, which have an area many times that of the surface of the particles. In the wet process of manufacturing superphosphate, apatite, as compared with phosphorite, requires about three times as long for the chemical reactions to be completed.

Gray⁶ estimates apatite and phosphorite production in all of Russia for 1939 as 2,137,450 metric tons, but this seems small in view of production at Kola. Accurate data on Russian deposits and production are unavailable.

Island Deposits

There are many deposits of phosphorites on islands in the Pacific Ocean, the Indian Ocean, and the Caribbean Sea. These deposits are alterations of coral limestone by seepages over long periods of time of phosphoric acid solutions from guano (bird excreta) deposits. Most of these islands are volcanic eruptions of molten lava, generally basic and quickly cooled. The part of the eruptive cone above the ocean surface was gradually eroded away on these small islands before the coming of the zoophytes, the organisms that deposit coral (calcium carbonate) on rocks under the ocean.

By erosion, the eruptive cone then became a truncated cone with its flat top just at or below the ocean water level. The coral was then deposited as a "collar" around, or as a cover over, this island. Later, the level of these islands was raised, and still later there came colonies of marine birds, which used such coral islands as homes, probably for centuries, and on them accumulated large deposits of guano. Seepage from rain water through the guano settled to the coral, and as these seepages contained phosphoric acid dissolved from the guano, the coral became altered from calcium carbonate to tricalcium phosphate.

Where there was no intermixture of detritus from the erosion of the basic lava, the grade of this phosphorite is very high, usually over 80 pct BPL. On some islands, where the coral was in the form of pinnacles, much lava detritus, now resembling soil, is mixed with the phosphate, sometimes greatly diluting it with iron and aluminum compounds, resulting in a phosphate sand running as high as 35 pct I&A and containing only 35 to 40 pct BPL. Such a phosphate can be used only for direct application to the soil.

Depending on the type of the island deposit, mining is carried on by quarrying, by dredging, and by "post-hole" digging of the phosphate in holes in the coral.

Japan carried on mining operations on many of her mandated islands received from Germany after the first World War—Fais, Peleliu, Angaur, Sonsorol, Tobe, of the Carolines group; Rota, Saipan, Tinian, of

the Marianas group; Okina Daito and Kita Daito, of the Ryukyu group; Ebon, of the Marshall group; and many other small islands that produced unimportant tonnages.

In 1945, when Japan surrendered, these islands had stock piles of mined wet rock ready to be dried (where possible) and shipped, amounting to 258,000 tons. Unmined reserves on these islands were estimated at 2,760,000 tons in 1946. Of these reserves, Kita Daito had about 1,400,000 tons, Angaur 800,000 tons, and Fais 200,000 tons.

In 1933, these islands produced for Japan 98,718 tons. Shipments rose to a maximum of 322,236 tons in 1939 and then gradually fell off to 171,000 tons in 1943, ceasing entirely after about 36,000 tons had been shipped in 1944. At peak production, these islands supplied only one third of the phosphate rock required in Japan for its very intensive agriculture.

Because of this urgent need of phosphates in Japan, General Douglas MacArthur late in 1945 asked for shipments of phosphate rock from the United States and the resumption of production from these islands, all of which at the time were under U. S. Navy control. The Japanese had efficient drying plants and equipment on only four of these islands—Angaur, Fais, Rota, and Kita Daito—but they were destroyed or badly damaged by bombing as the Pacific front advanced from Guam outward. However, the Navy had started phosphate production by June 1946 and shipped the first cargo of phosphate (wet rock) from Angaur in August 1946. By June 30, 1947, about 140,000 tons had been shipped to Japan from Angaur. Upon completion of repairs to plants and loading piers, annual shipments from these islands could be expected to reach a maximum of about 700,000 tons, quickly falling off as the reserves become exhausted at Angaur and Fais.

Before the war, Japan consumed more than 800,000 tons of phosphate rock annually, so that 75,000,000 people could be fed from her agriculture on her relatively small islands, having an area of only about one fourth more than the British Islands (including Eire), whose population is only about 45 million.

In the Gilbert group, are the British islands of Nauru and Ocean^{4,6} just south of the equator near longitude 167°E. On these two islands are sizable deposits of phosphate. They are operated by the British Phosphate Commission for the joint account of Great Britain, Australia, and New Zealand. Practically all the phosphate mined since World War I has been shipped to Australia and New Zealand but a small tonnage was shipped to Japan at times.

In 1940, Ocean and Nauru shipped 1,263,000 tons, of which Nauru produced about 1,000,000 tons. The production from these islands is of very high grade, being 83 to 87 pct BPL.⁹

The mines are modernly equipped and well managed. At Nauru,

a splendid cantilever loading pier loads vessels at a high rate and cheaply. Unfortunately, this pier was badly damaged by the Japanese in 1942. Since Japan's surrender, the equipment on these islands is being rehabilitated but production had not reached normal by 1946.

On Makatea Island, of the Society group, the Anglo-French Phosphate Co. owns an important deposit of phosphate. Mining started on this island in 1911. Shipments grade very high, about 83 to 85 pct BPL. In 1944, it was estimated that Makatea shipped about 200,000 tons.

In the Indian Ocean is Christmas Island, southwest of Java. This island, belonging to the British, became a producer in 1899 and in 1940 its output was 242,000 tons. Its production undoubtedly suffered during the war but no data are available as to its output after 1940. Shipments were of very high grade, 85 pct BPL.

In the Caribbean Sea, the most important deposit is that of the Dutch Island of Curaçao, off the coast of Venezuela. There were two deposits on this island, one of very high grade, 85 pct BPL, and the other of 77 pct BPL. Mining operations started probably in 1871 but its production was not important in the early days and there were many shutdowns. However, after World War I, production generally exceeded 100,000 metric tons annually and was of high grade. In the early 1930s, apparently the higher grade deposit became exhausted and shipments dropped to 77 pct BPL.⁶

In 1938, exports from Curaçao reached 104,000 tons, dropping to only 6,000 tons in 1940 but recovering the next year to 112,000 tons. Later figures are not available.

Other small islands of the West Indies, such as Aruba, Redonda, Sombrero, Navassa, have produced phosphate in the past but are today unproductive, or their production is small and for local consumption.⁶

Other Phosphate Deposits

The geographical groups of phosphate deposits that have been mentioned cover the largest and most important producing areas that are, or have been, engaged in the world phosphate-rock trade. Almost all countries have mined small tonnages of phosphate rock within their borders for local consumption. There is hardly a country in Europe not in this class.

In North America, there are known deposits of phosphate rock in Canada and in Mexico. In South America, deposits are being worked for domestic consumption in Chile, in Brazil, and possibly in French Guiana. Australia and New Zealand produce some phosphates but their large demands are satisfied only by importations from Ocean and Nauru Islands. Deposits have been found in China and Indonesia, and it is reported that the Soviet has found two large deposits in Asiatic Russia. There is said to be an extensive deposit in Transjordan, in

the mountains to the east of Jerusalem. Other deposits in Africa are known in Senegal, Tanganyika, Nigeria, North Transvaal, and Cape Colony.

WORLD PRODUCTION OF PHOSPHATE ROCK

World production of phosphate rock will continue to increase as world populations increase, because man's civilization seems to require about half of his number living in large cities and being fed by the rest. Phosphate-rock production would double today if the farmer were to put back into the soil each year the phosphate that is lost to the soil by cropping. It would probably treble if, in addition, he gave the soil that which is lost by erosion and for other reasons.

Today, even in countries proud of their intelligence and their productive ability in agriculture, the phosphate lost to the soil by cropping is not being replaced. In 1944, for instance, the 25 states west of Michigan, Pennsylvania, West Virginia, Kentucky, Tennessee, Mississippi and Louisiana,³ removed more P_2O_5 from the soil by cropping than was returned to the soil in the fertilizer applied. The other 23 states not only put back the P_2O_5 lost by cropping but, in addition, more than $1\frac{1}{2}$ times as much more. It is interesting to note that if the 25 states to the west had replaced only the P_2O_5 lost by cropping in 1944, they would have applied the equivalent of over 3,500,000 tons of 72 pct BPL phosphate rock instead of the equivalent of only about 1,000,000 tons that was actually applied to the soil. In addition, if $1\frac{1}{2}$ times more in excess were applied, as was done in the other 25 states, they would have applied the equivalent of almost 9,000,000 tons of 72 BPL phosphate rock. This would have brought the 1944 consumption of phosphate rock in the United States up to about 12,000,000 tons as compared with a consumption slightly over 5,000,000 tons. The same is true for many countries in the world.

Economic depressions and wars also affect the production and movement of phosphate rock. In depressions, the farmer is forced to curtail his production, for his market diminishes and in turn he buys less fertilizer. In wars, transportation of phosphate rock becomes badly upset. Such conditions cause dips in the world production curve for phosphate rock, but they are temporary. The curve *must* go up.

World production of phosphate rock in 1939 was estimated at about 12,000,000 metric tons. In 1940, it had dropped to about 10,000,000 tons. For the years 1941 to 1944, there are not sufficient data available, but production probably dropped to as low as 8,000,000 tons. In 1947, it probably recovered to a high of almost 19,000,000 metric tons.

Table 1 gives available figures on production of phosphate rock in various countries in recent years.

TABLE 1—*World Production of Phosphate Rock, 1940, 1943 and 1945, by Countries^a*
METRIC TONS

Country ^b	1940	1943	1945
Algeria.....	370,890	76,798	401,304
Australia:			
New South Wales.....	20	122	
South Australia.....	254	12,976	725
Western Australia.....	39	43	8,619
Austria.....	^c	^c	^c
Belgium.....	280	108,900	17,990
Brazil (apatite).....	^c	6,111	^c
Canada.....	325	1,316	271
Chile (apatite).....	32,000	37,924	13,203
Christmas Island, Straits Settlements (exports).....	241,826	^c	^c
Egypt.....	183,464	315,566	349,374
Eire.....	^c	17,252	^c
France.....	24,260	131,020	60,622
French Oceania (exports).....	164,170	188,385	259,000
Germany.....	1,548	^c	^c
India.....	119	1,215	532
Indochina, French:			
Phosphate rock.....	24,340	19,890	
Apatite.....	2,070	64,600	^c
Italy.....	274	^c	^c
Japan ^d	1,400	1,200	2,000
Madagascar.....	495	^c	^c
Morocco, French.....	687,310	806,171	1,154,120
Nauru and Ocean Islands ^e	1,263,385	^c	^c
Netherlands Indies.....	34,085	24,000 ^f	^c
Netherlands West Indies:			
Curacao (exports).....	6,047	^c	8,770
New Zealand.....		9,389	8,084
Palestine.....	^c	5,384 ^g	4,867 ^g
Rumania.....	95	^c	^c
Seychelles Islands (exports).....	14,613	1,849	7,090
South-West Africa.....	869	164	27
Spain.....	15,781	15,722	20,349
Sweden (apatite).....	7,479	144,265	^c
Tanganyika Territory.....	9	269	^c
Tunisia.....	1,187,823	334,678	706,404
Union of South Africa.....	^c	5,801	^c
U. S. S. R. (apatite).....	2,600,000	^c	^c
United States (sold or used by producers).....	4,066,943	5,208,508	5,899,921
Total ^h	10,933,000	7,540,000	8,924,000

^a Compiled by B. B. Mitchell. Minerals Yearbook, U. S. Bureau of Mines.^b In addition to countries listed, Angaur Island, China, Formosa (Taiwan), New Caledonia, and Republic of the Philippines produce phosphate rock, but data of output are not available.^c Data not available.^d Preliminary data for Noto Peninsula, Honshu, for fiscal year ended March 31 of year following that stated.^e Exports during fiscal year ended June 30 of year stated.^f Estimate.^g Exports.^h Totals represent only those countries for which statistics are shown.

WORLD RESERVES OF PHOSPHATE ROCK

World reserves of phosphate rock were estimated by the American Phosphate Rock Institute in 1938 to be 17,464,357,000 metric tons, of which 7,370,950,000 tons were in the United States. However, Mansfield¹¹ in 1942 estimated the United States reserves at 13,291,543,000 tons, which would increase the world estimate to more than 23,000,000,000 tons. Even if this is all the phosphate rock remaining, discovered and undiscovered, and even though the world consumption of phosphate rock doubles, there appears to be enough phosphate rock to last us 600 years.

PRICES

Typical prices of phosphate rock are indicated in Table 2.

TABLE 2—*Typical Prices of Phosphate Rock in 1947^a*

PER LONG TON UNGROUND, WASHED, AND DRIED PHOSPHATE ROCK, IN BULK F.O.B. CARS
AT MINE

Grades BPL Content, Pct	Florida Land Pebble		Tennessee Brown Rock
	Jan. 13, 1947	Dec. 29, 1947	
68/66	\$2.60	\$3.34–\$3.49	\$5.50 6.00
70/68	3.00	3.74– 3.89	
72/70	3.60	4.34– 4.42	
75/74	4.60	5.34– 5.49	
77/76	5.60	6.34– 6.49	

^a From *Oil, Paint and Drug Reporter*.

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CHAPTER 34

POTASH*

By HOWARD I. SMITH†

POTASH is of prime importance as a plant food and is also widely used in industry. The term "potash" was applied to a crude pearlash obtained by evaporating, in iron pots, solutions leached from plant ashes. Later it included caustic potash obtained by treating pot ashes with lime, and now it is applied generally to various compounds of potassium used by agriculture and industry. Herein it applies to the theoretical equivalent in potassium oxide (K_2O)—a compound never found in nature or manufactured in commerce but generally used as a common denominator for comparison of all potassium compounds. Potash was made from plant ashes at an early date, but potassium in mineral form was not noted until 1797, when it was identified in leucite.³ The importance to plant life of potash in the soil was first recognized by von Liebig³ and his published reference thereto appeared in 1840. In 1843, potash was discovered in the brine of a well drilled for salt near Stassfurt.

HISTORY OF THE AMERICAN POTASH INDUSTRY

Among the colonists reaching Virginia in 1608 were men from Poland skilled in making potash from wood ashes¹⁹ and records show that the production of potash was begun in other colonies also, soon after their establishment. The American product entered the trade in 1635, and at various times since that date the production of potash for industry has been subsidized by the Government or protected by tariffs.

The production of potash from wood ashes reached its peak in 1825. Beginning in 1823, a cheaper product, sodium carbonate, made by the Leblanc process, was substituted for much of the potash used in industry. Production rapidly declined after the Civil War, when the forests most productive of potash had become depleted and labor had become

* Published by permission of the Director, U. S. Geological Survey.

† Chief, Mining Division, U. S. Geological Survey, Washington, D. C.

The writer is indebted for assistance in the preparation of this chapter to T. F. Stipp, U. S. Geological Survey; H. M. Albright, President U. S. Potash Co.; G. F. Coope, President, and W. E. Douglas, Research Director, Potash Company of America; A. R. Merz, principal commodity specialist, U. S. Tariff Commission, and to Miss Cornelia M. Nelson, U. S. Geological Survey.

more profitably employed, with the improvement of transportation facilities that permitted the marketing of timber, farm products, and livestock. Furthermore, the development of natural potash salts from saline deposits in Germany began in 1861, an educational program devised to stimulate the use of potash as a fertilizer followed, and German production increased rapidly.

The need for a domestic source of potash for agriculture did not appear urgent until 1910, when certain contracts for the purchase of foreign potash, favorable to American fertilizer manufacturers, were canceled, and the extent of American dependence on foreign potash, particularly for agriculture, was recognized. In 1911 an extensive search was begun by several Government agencies,³⁴ which, together with prospecting by private interests, led directly to the establishment of the present potash industry, chiefly at Searles Lake in California and in Eddy County, New Mexico.

COMPOSITION OF POTASH MINERALS

The composition of the five potash minerals occurring in greatest abundance in the Permian saline deposits is as follows.

EQUIVALENT	PERCENTAGE K ₂ O MINERAL
Sylvite (KCl)	63.2
Langbeinite (2MgSO ₄ .K ₂ SO ₄)	27.7
Polyhalite (K ₂ SO ₄ .MgSO ₄ .2CaSO ₄ .2H ₂ O)	15.6
Carnallite (KCl.MgCl ₂ .6H ₂ O)	16.9
Kainite (MgSO ₄ .KCl.3H ₂ O)	18.9

Fifty other minerals from Permian saline deposits³⁰ and 11 additional minerals from the Searles Lake deposits in California¹² have been identified.

The composition of four other potash minerals of interest, each from a different type of deposit, is:

MINERAL	PERCENTAGE K ₂ O EQUIVALENT
Niter; saltpeter (KNO ₃), cave, caliche, or playa deposits	46.5
Alunite [K(Al) ₃ (SO ₄) ₂ .3H ₂ O], hydrothermal deposits	11.4
Orthoclase (K ₂ O.Al ₂ O ₃ .6SiO ₂), magmatic deposits	16.9
Leucite [KAl(SiO ₃) ₂], lava deposits	21.5

PROPERTIES

The element potassium, according to Brewer,⁵ has three isotopes of masses 39, 40, and 41 in the proportion of 8300, 1, and 585, respectively. K⁴⁰ is the radioactive isotope with a ratio of beta to gamma rays of 100 to 1. The ratio of K³⁹ to K⁴¹ varies in different plants, animal tissue and bones, but the significance of the variation has not been determined. Some success has been had in the concentration of the

isotopes of potassium⁶ that presents an opportunity for a new field of research.

Spicer,³⁶ in his studies of the gamma ray, shows that it may be used to determine the percentage of potassium present in potash minerals and illustrates its possibilities for the logging of holes drilled for potassium salts.

Sylvite is isometric, hardness 2.2, specific gravity 1.98, luster vitreous, cleavage cubical, color clear to milky white to brick red. In taste it is similar to halite but it has a quicker or sharper taste and a cooling effect on the tongue. After tasting several pieces, however, it is difficult to distinguish it from halite by this means. It is very plastic under pressure and, with unrestricted sides, a halite-sylvite mixture can be compressed 60 pct¹⁴ and still maintain the initial bearing strength per square inch. This is an important factor in mining and must be considered in selecting fine-grinding equipment. The sylvite mined in New Mexico contains some water that is squeezed out when the ore is compressed. When the ore is dissolved, bubbles of gas, probably nitrogen, are given off.

Small quantities of blue halite usually occur in association with sylvite and rarely elsewhere. The origin of the coloring has not been determined.

Langbeinite is isometric, hardness 4.2, specific gravity 2.82, luster vitreous, fracture conchoidal, and it has no cleavage. It ranges from clear to gray in color and is tasteless, somewhat granular, and slowly soluble in water. After exposure to the atmosphere for some time, the outside of the specimen is altered to a white powder, probably leonite and epsomite, which in isolated crystals brings out their triangular shape in contrast to those of the associated halite or anhydrite.

Polyhalite is triclinic, hardness 3.6, specific gravity 2.77, luster dull. It ranges in color from white to brick red, is normally opaque and rarely translucent, and has no taste. It is massive and breaks with a conchoidal fracture. Coarsely ground material is very slowly decomposed by water at ordinary temperature. It can be distinguished from anhydrite by its white coating of gypsum after wetting and drying. Anhydrite is not dissolved by wetting and retains its natural color on drying. Polyhalite was the first potash mineral identified in the Permian salts in New Mexico but it is not being mined anywhere at this time.

Carnallite is orthorhombic, hardness 2.7, specific gravity 1.60, luster vitreous, fracture conchoidal, color clear to white to reddish brown, and it has a sharp, bitter taste. It is highly hygroscopic and shipments containing carnallite cake badly in transit or storage. It was the first potash mineral to be mined from saline deposits in Germany.

Kainite is monoclinic, usually granular, hardness 3, specific gravity 2.13, ranges in color from white to dark flesh red. It was the second

potash mineral to be mined from saline deposits and is still mined in small amounts in Europe. However, it has little relation to the fertilizer sold as kainite, which is a mixture of salts with low potash content.

Orthoclase is monoclinic, hardness 6, specific gravity 2.57, luster vitreous, translucent, ranges in color from white to pale yellow, also red and green.

ORIGIN AND MODE OF OCCURRENCE

The occurrences of potassium in nature are as varied as its uses. It is found in rock and saline deposits and in the waters of lakes, rivers, and oceans. Clarke⁷ estimates that 3.11 pct of the earth's land surface is composed of potash and that the waters of the oceans contain nearly 0.05 pct. Much of the potash occurs in chemical compounds that have no present economic value. The most easily available and usable form of potash is the mineral sylvite. Sylvite and associated minerals are believed to have resulted from the evaporation of saline waters of an arm of a sea or a large saline inland lake, in a hot, arid climate. The salts, principally sodium chloride, thus selectively precipitated, were covered by sedimentary rocks, such as clays, shales, limestones, and sandstones. The deposits of soluble potash mined in the United States, central Europe, and Russia occur in the Permian series; in Alsace, France, in the Oligocene; in Poland in the Miocene; and in Spain in the Tertiary.²²

The extent of the Permian salt basin in the United States has not been clearly defined but in general it includes parts of Colorado, Kansas, Oklahoma, Texas, and New Mexico. As early as 1887, Hill¹⁶ directed attention to the enormous deposits of salt and gypsum in what was known as the Permian Basin, though not then fully accepted as such, and also to the fact that its deepest part was not far from its southern border. The salt series of the Permian Basin in New Mexico and Texas has thus far yielded no fossils;²¹ however, the succession of anhydrite and halite with the more soluble minerals in spongelike masses of halite, though complex, indicates sea water as the primary source of the deposits. The repetition of beds of clay, anhydrite, and halite further indicates that the cycle of evaporation and deposition was interrupted and renewed many times.

In New Mexico, sylvite, langbeinite, and carnallite have been found in important quantities only on the western flank of the basin where it rises to an old erosion surface now buried some hundreds of feet by later sediments. After the deposition of much of the salt series, mineralogic changes were induced by continued reactions of the salts with the mother liquors, as has been ably illustrated by Schaller and Henderson.³⁰ Because the gradual withdrawal of the Permian Sea was toward the southwest, the salt deposits in southeastern New Mexico are

younger than those to the north and their richness is attributed in part to the concentration of the residual brines.

The southern part of the Permian Basin in New Mexico and Texas is a broad, asymmetric syncline, trending generally northeastward and characterized by gentle dips on the east and steeper dips on the west. The Delaware Basin, an arm of the Permian Basin in southeastern New Mexico and adjoining parts of Texas, is pear-shaped in outline and contains the greatest thickness of upper Permian rocks in the Southwest. Apparently it resulted chiefly from the combined effects of reef building and structural warping. Its rim is formed by the Capitan dolomitic limestone.

In the central part of the Delaware Basin, in Lea County, New Mexico, about 1000 ft of salt is found through a stratigraphic thickness of as much as 4000 ft, divisible into a lower salt series (Castile anhydrite) and an upper salt series (Salado halite). These saline beds, cut off by erosion in the valley of the Pecos River on the west, thin out toward the other boundaries of the basin.

The Castile anhydrite, or lower salt series,²² consists of gray anhydrite, relatively clean white rock salt, some sandstone, and dolomitic limestone. Commercial amounts of potash have not been found in this series.

The Salado halite, or upper salt series, is made up of pinkish to white rock salt, reddish and shaly sandstones, and anhydrite, which in places is replaced by polyhalite. The upper part of this series contains local concentrations of chloride and sulphate salts of potassium, such as occur about 20 miles east of Carlsbad, New Mexico.

Polyhalite has been found in the southern portion of the Permian Basin in an area of about 40,000 square miles.²¹ Sylvite, carnallite, or langbeinite has been identified in cuttings from holes drilled for oil and in cores from test holes drilled for potash in an area of 3000 square miles lying in southeastern New Mexico and extending into Texas (Fig 1).

It is reasonable to expect that the area of known potash reserves may be extended or that other such areas may be discovered as additional information is obtained from drilling and from geophysical prospecting. The 3000-square-mile area is bounded in part on the east by the Capitan reef, here extended beneath cover, and on the west by the eroded and covered edge of the Salado halite. Of the three developed areas, one is north and two are south of the Capitan reef. Potash salts, other than polyhalite, have also been found north of the San Andres reef zone (Fig 1), which lies at some depth below the salt series and to the north of the Capitan reef.

The area intensively tested by core drilling is shown on the 15-minute topographic map made by the U. S. Geological Survey of the potash

mines area that extends 25 miles northward and 15 miles eastward from Loving, New Mexico. The correlation of one hole with another in this area is simplified by reason of a persistent zone of white polyhalite that occurs a few feet above a prominent anhydrite zone. As this sequence occurs also at two horizons in the southern part of the area, without a study of the entire series some confusion may result.

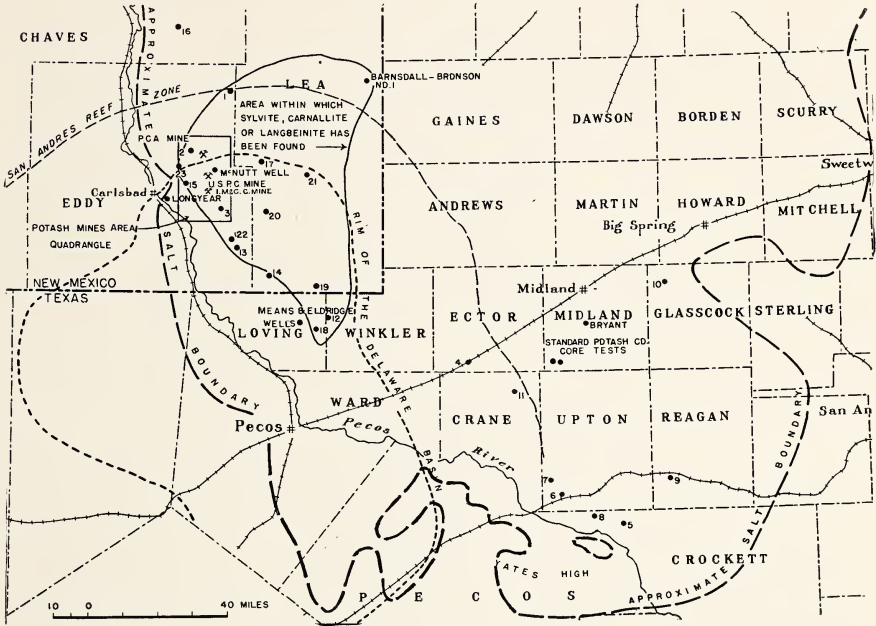


FIG 1—SOUTHERN END OF PERMIAN BASIN IN NEW MEXICO AND TEXAS.

Compiled after maps by Mansfield and Lang,²² supplemented by unpublished information on Pecos County, Texas, from B. R. Haigh, Texas University Lands, Midland, Texas. Shows location of Longyear well,²⁰ where the first core test was made in the Permian Basin for potash exploration, 1917; Bryant well,³² from which the first polyhalite in the Permian Basin was identified, 1921; McNutt well,²³ where sylvite was first discovered in the Permian Basin in 1925; Barnsdale-Bronson No. 1 well, the northernmost well showing soluble chlorides of potash; Standard Potash Company's two core tests.⁴⁴ Means well, drilled in 1921, is located near the thickest part of the salt series. It was offset by Eldridge core test, the first well core drilled for potash in Texas, completed in 1926. Nos. 1 to 23 indicate Government core tests drilled for potash in 1926–1931.²²

A correlation, based on the McNutt No. 1 well supplemented by later drilling, shows enrichment of potash in 40 zones, here called beds.³² Beginning at the top potash bed in the McNutt hole, designated No. 1, beds 1 to 16 are classified as polyhalite beds; however, the percentage of polyhalite and anhydrite varies in the cores from the different holes. In beds 17 to 28, sylvite predominates except in bed 23, where white polyhalite predominates, and in bed 24, where anhydrite predominates.

Correlation in the field is based on these two beds. The only potash mineral found below bed 29 is polyhalite. Other potash beds probably occur to the east above the bed herein termed No. 1 and in places other beds occur among some of the 40 beds used for correlation.

The beds are not uniform in lithology, thickness, or intervals of succession, and few of them, if any, are continuous throughout the area. The most promising core test of polyhalite showed one bed 9 ft thick containing 13.5 pct K_2O . Bed 24, generally recognized as anhydrite throughout the area, in places contains a high percentage of polyhalite. Carnallite is found in greatest abundance in bed 17 and langbeinite in beds 22 and 25. Each of the beds numbered 17, 18, 25, 26, and 28, as at present indefinitely outlined, includes areas of sylvite, carnallite, or langbeinite more than 4 ft thick, with a potash content of 14 pct or more. Sylvite is mined from bed 28 by all three of the producers in New Mexico and langbeinite is mined from bed 22 by one producer. Kieserite, which abounds in Europe, is widely scattered in small quantities through the Salado halite. Occasionally salt horses¹ like those that occur in European potash mines occupy areas varying in size, and failure to find potash in a core through a particular horizon is not conclusive evidence that rich salts may not be found near by.

The Searles Lake brines in California occur in a spongelike salt deposit resulting from the evaporation of inland waters. Mining claims for borax, soda, and potash were located in the salt flat as early as 1898 by Whitman Symmes but not until February 1912 was it publicly announced that the brines were a potential source of potash. They are also an important source of borax, soda ash, salt cake, and bromine and lithium salts, and a potential source of tungsten.

The Bonneville flats²⁵ brines in western Utah consist primarily of sodium, potassium, and magnesium chloride at shallow depths.

DISTRIBUTION OF DEPOSITS

United States

Many sources of potash exist in the United States, some of which were put into production during World War I. In 1918, the year of greatest production during that period, the brine deposits of Nebraska, Utah, and California furnished 73 pct of the domestic production, kelp 9 pct, molasses distillery waste 6 pct, alunite 5 pct, and cement and blast-furnace dusts, beet-sugar water, wood ashes, wool washings, and other sources 7 pct. During 1946, the three mines in southeastern New Mexico and the brine plants in California and Utah supplied most of the domestic production. Small quantities of potash were recovered from brine wells near Midland, Michigan, from alunite at Marysville, Utah, and from the dust from a cement plant at Security, Maryland.²⁴

That the salt deposits in the Paradox Basin in eastern Utah and

western Colorado contain a large reserve of potash salts is indicated by analyses of cores and cuttings from 17 wells drilled in the area,¹⁰ but, because of the depth to the salt horizon and the folding of the formation, activities in the area have been confined to prospecting.

The deep-seated saline mineral deposits are the chief source of potash. Such deposits are now being worked in the United States, Germany, France, Spain, Russia, and Poland.

Other Countries

The German deposits nearly encircle the Harz, Flechtigen, and Thuringer Wald uplifts, underlie the intervening basins, and extend northwest under the Hanoverian lowlands and southwestward into Thuringia, embracing a potentially productive area of possibly 24,000 square miles. The deposits worked may be divided into six districts: Werra-Fulda; South Harz (including Wuesfurter and Mansfelder trough); North Hanover and North Harz; Magdeburger-Halberstadt-Stassfurt Basin; lower Rhine near Wesel; and the border district in Baden. Potash production in 1944 was 1,925,000 tons and in 1946 it was 955,400 tons.

Potash was first discovered in Alsace about 21 miles northwest of Mulhouse, France, in 1869. The deposits now being worked, however, were discovered in 1904 in drilling an exploratory hole for oil. The discoveries in other holes subsequently drilled warranted development, and in 1909 the first shaft was completed; in 1910, 37,000 metric tons of crude salts was mined. The deposit lies in a graben along the Rhine River, about 25 miles north of the Swiss border and 375 miles by river from Rotterdam. The river alluvium is underlain by shale, rock salt, gypsum, or anhydrite, and other deposits, indicating deposition from evaporation. The upper bed, 3 to 5 ft thick, contains about 21 pct K_2O and covers about 84 sq km (32 sq miles). The lower bed, 10 to 16 ft thick, averaging 12 to 15 pct K_2O , covers 172 sq km (66 sq miles). The reserves are estimated, in round figures, at an equivalent of 300,000,000 tons K_2O ,²⁹ and production in 1947 was 714,000 tons.

A new potash mine near Dax, south of Bordeaux, France, with a daily production of 100 tons was reported in 1947.

The Spanish deposits lie about 60 km from Barcelona, between the Pyrenees Mountains on the north and the Catalanian Ridge on the south, in an area about 75 miles long with a maximum width of 15 to 18 miles.¹⁷ The three mines are near Suria, Sallent, and Cardona, and plans for the development of a mine near Pamplona in Navarro Province are reported. Potash production in 1947 was 153,809 tons.

The Russian deposits near Solikamsk—where prospecting began in 1916, development in 1925 to 1927, and production in 1930—lie on the west side of the Ural Mountains, on the Ussolka River, a branch of the

Volga, about 200 km from Perm, on the Kama River, 1800 km from Leningrad, and 2000 km from the Black Sea. The explored deposits extend about 30 km north and south and 10 km east and west. One mine is in the northern section in the vicinity of Solikamsk and another is in the southern section in the vicinity of Berezniki. The production of crude salts from these deposits during 1937, the last year for which figures are available, was reported as 2,400,000 tons, equivalent to 266,000 tons of potash.

The Polish deposits, now held by the Soviet Union, although discovered in 1854 and first exploited in 1862, yielded but little potash prior to 1920. They lie north of the Carpathian Range, extending from Kalusz to Stebnik, a distance of 70 km, in a belt 3 to 4 km wide, and are developed through three mines at Kalusz, Holyn, and Stebnik. Potash production in 1938 was 108,000 tons.

The reported discovery of sylvite in western Canada was confirmed Feb. 19, 1947, by the Resources Minister of Saskatchewan. The discovery was made in drilling for oil and available information indicates that the salt deposit cut in drilling lies in a flat arc extending from Radville, about 40 miles north of the Montana-North Dakota line, to Unity in Saskatchewan, to Elk Point in Alberta, a distance of about 450 miles. Potash was identified in one hole about 10 miles northwest of Unity, one hole 30 miles northwest of Radville, two holes midway between Moose Jaw and Saskatoon, and one hole 25 miles northwest of Swift Current. The most promising discovery is near Unity, where a deposit 11 ft thick of 21.5 pct K_2O was reported at a depth of 3466 ft. Other discoveries have been reported in Nova Scotia but as yet the deposits are undeveloped.

The discovery of a deposit of potash in North Yorkshire, England, was made in 1946 in prospecting for oil but at such depth that it was not prospected further.

In 1947, a discovery of potash in the Saldrup salt dome in Jutland, Denmark, was reported but the significance of the discovery has not been revealed.

The principal foreign brine deposits are those of the Dead Sea, in Palestine, now being worked by the British. They yield bromine as well as potash. In 1946, a production of 45,300 tons of potash was reported.

A persistent effort has been made by Italy to produce potash from sea water and as late as 1930 potash was produced from saline springs and brine wells in Ethiopia on lands held under an Italian concession obtained in 1914. This Ethiopian potash was an important source of supply to the Allies during World War I.

Potash is obtained in small quantities from various sources in many countries. It is produced from kelp in the British and Japanese islands;

bitartrate is produced from wine lees in a number of countries; potassium nitrate is derived in relatively small amounts from sodium nitrate deposits in Chile and elsewhere. Chile produced 64,838 tons of crude salts in 1943. Alunite was a source of aluminum in Korea and Japan during World War II and potassium alum was derived from alunite in Australia. A production of 36,427 tons of potassium salts in Australia was reported in 1946.

Reserves

The potash reserves of the United States, according to Dolbear,⁹ exceed 100,000,000 tons. Dolbear bases his estimate on deposits of sylvite, langbeinite, and carnallite, more than 4 ft thick and having a potash content of not less than 14 pct, and on the brines of California and western Utah. In addition, reserves of polyhalite, greensands, wyomingite, and Georgia shales exceed 1,000,000,000 tons. Turrentine⁴³ gives the world reserves of soluble salts and brines at about 5,000,000,000 tons, but the bases used by the representatives of the various countries that made the estimates were not revealed by them. However, world reserves sufficient for centuries to come appear to be assured.

POLITICAL AND COMMERCIAL CONTROL

The production of potash from saline mineral deposits has always been under varying degrees of political control. The Heydt and Mantuffel companion shafts sunk near Stassfurt for the production of rock salt by the Prussian Government initiated the production of mineral potash late in 1861. During 1856 and 1857, in sinking these shafts, several hundred tons of potash salts was thrown on the dump as worthless; however, some of it was sold for agricultural purposes. The Leopoldshall shaft, developed by the Duchy of Anhalt, began to produce potash in 1862. For the next 13 years, production was confined to those two state-developed properties. The first mineral mined was carnallite.

The two producers agreed on a price for crude salts but the manufacturing branch of the industry, a private affair, increased the number of factories from 3 in 1862¹⁷ to 18 in 1865, and competition developed not only among the potash factories but between potash and soda ash. This competition resulted in a decline in prices for 80 pct KCI from 320 marks (about \$76) a ton in 1863 to 149.60 marks in 1865, which caused 5 of the 18 refineries to go bankrupt and others to change hands.³⁷ By 1869, the price had risen to 175 marks but by 1873 it had reached a new low of 120 marks. Financial casualties resulted and in 1876 the first potash syndicate was formed, which was little more than an association for weekly price agreements. The syndicate seems to have been dissolved a year later and by 1878 the price of muriate was only 95 marks.

With the beginning of intensive commercial development, Prussia

adopted a new mining law on June 24, 1865, which was soon followed by similar laws in most of the other German states. These laws recognized freedom in prospecting by anyone anywhere on application to the surface owner for permission to prospect, and, after a discovery of potash, the owner could be forced, on application to the district mining official, to grant a concession for exploitation.

The first private development was the Douglasshall mine, where two shafts sunk near Westeregeln were completed in 1873 and 1874 and operations were begun in 1875. The Salzbergwerks followed in 1877.

The long-established idea of state control of industry led the Prussian Fisc in 1877 to endeavor to unite the two state-controlled and the two private enterprises under a working agreement for allocation of output and regulation of prices, but the two private operators refused to accept the proposed terms, which would have reduced their output.

An agreement was reached in 1879, marking the first potash cartel, which in effect limited the output of carnallite for 5 years, determined its distribution to refineries, and regulated certain prices. The kainite producers entered into a similar agreement. The muriate factories fixed the prices for the concentrated products and in 1883 formed an association for marketing their products through a central sales office. Until 1910, the cartel was a rather loose organization depending on term agreements. A discord arose between those wishing to maintain prices and those promulgating the policy of lower prices and larger sales, and, as no agreement had been reached by midnight of June 30, 1909, the last day of the agreement then in force, all were free to make individual contracts. Within a few hours the Schmidtman and Westeregeln group made contracts with American agents involving the equivalent of 120,000 tons of K_2O annually, at prices ranging from 30 to 40 pct below the syndicate price on 2-year contracts, with options on a 5-year extension. After considerable international negotiations, Germany finally, on May 25, 1910, enacted a law that obligated the Americans to surrender their contracts at a loss of \$25,000,000 on the contracts and to pay \$2,000,000 to \$3,000,000 in surtaxes to the German Government.¹⁷

The Schmidtman prices at that time were the prices at which, it is believed, several German mines could have produced at a profit. The Schmidtman and syndicate prices per metric ton for the several grades of salt c.i.f. Atlantic ports were, respectively, as follows: muriate, \$20.40, \$32.98; sulphate, \$25.80, \$38.80; double manure salts, \$14.14, \$20.37; 20 pct manure salts, \$7.13, \$11.64; hartsalz, \$5.72, \$8.73; kainite, \$5.16, \$7.03.

The law of 1910 was intended to control production in Germany through allotments but it promoted conditions it was intended to eliminate and the result was an orgy of sinking new shafts and the creation

of several new concerns or subsidiaries by establishing compacts to protect the allotments formerly enjoyed. By April 1911, the 69 syndicate mines were being increased by 79, and two years later 127 mines were operating and 132 under development, a total of 259 shafts.¹⁷ In 1945, according to East,¹¹ only 31 mines remained, some of which had not operated for several years. The consumers of potash paid for the folly of enacting laws that interfered with normal development and aggravated rather than remedied a bad economic situation.

German domination of world production and marketing of potash was terminated after World War I by the transfer of Alsace, with its potash mines, to France; the liberation of Poland and the increased rate of development of its deposits in 1922, and the beginning of production from the saline deposits in Spain in 1925, from Palestine brines in 1930, from the Russian deposits in 1930 and from the New Mexico deposits in the United States in 1931.

At present the Russian Army of Occupation controls 61 pct of the German potash production and all of the Polish production.

In the United States, there are three classes of ownership of potash lands: fee, State, and Federal. There is no political control of the industry but, to prevent a repetition in the United States of the experience in Germany from overdevelopment, the Federal Government in 1934 suspended action on applications for potash prospecting permits and leases on Government lands, except in particularly meritorious cases. There was no Government restriction on prospecting State or fee lands, coring for potash in wells drilled for oil on Government lands, or prospecting on leased Government lands. The issuance of prospecting permits was resumed in 1946.

The greater part of the known domestic potash reserves is on public lands now held under lease from the Government through the Department of the Interior. Supervision of operations, in accordance with the terms of the leases, is a function of the United States Geological Survey.

Through expansion of the production capacity of the three large mines in New Mexico and the brine plants in California, during World War II American producers were able to supply not only domestic needs but the critical needs of friendly nations. This expansion was accomplished by the expenditure of private capital and at the risk of the producers, without Federal or other public aid or increase in sales prices.

PRODUCTION AND CONSUMPTION

United States

Production, imports, exports, and values are shown graphically in Fig 2. The first mineral mined in the United States for commercial

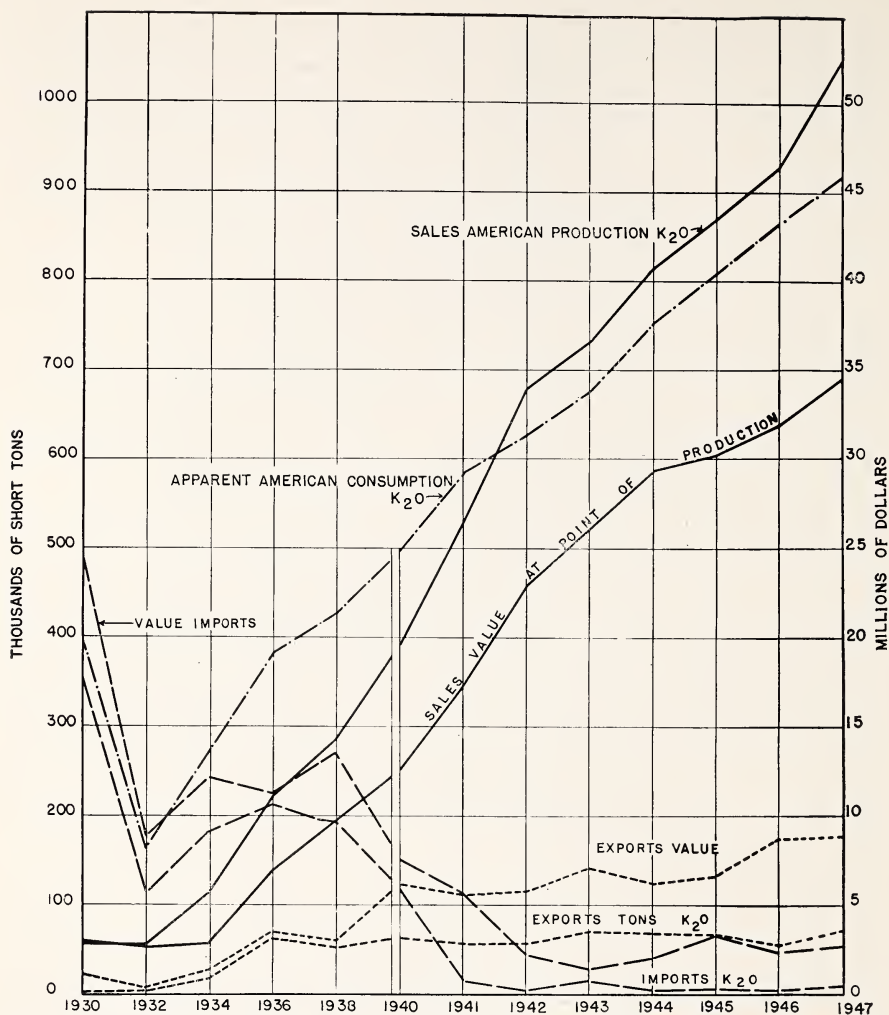


FIG 2—APPARENT CONSUMPTION AND TREND IN AMERICAN PRODUCTION, IMPORTS, EXPORTS, AND VALUES, 1930-1947, POTASH MINERALS.

Figures on the right refer to value; on the left, to short tons.

production of potash was alunite, in 1915. Brines, cement dust, ashes, and kelp also contributed to the 1915 production of 1090 tons of pure potash. Owing to the demand for domestic potash induced by World War I, by 1918 production had increased to 54,805 tons, or about 20 pct of the domestic requirements. Of this amount, 53 pct came from shallow lakes in western Nebraska, 34 pct from California, 7 pct from Utah, and 6 pct from 19 other states.

As German potash again became available, American production declined and in 1921 reached a low of 10,171 tons. By 1930, it had in-

creased to 61,270 tons, owing principally to increased production from Searles Lake brines in California, which began in 1916.

Production from the Bonneville flats, near Wendover, Utah, started in 1917, was discontinued in 1931 and was resumed in 1937 when a new plant was constructed. The process now used consists of pumping the shallow brines into solar-evaporation ponds and separating the KCl from the salt by flotation.

Production in New Mexico, which began in 1931, followed 5 years of intensive prospecting that has continued to date. The increase in production and the increase in efficiency in the recovery of potash from the three mines in New Mexico and the brine plants at Searles Lake, California, and Wendover, Utah, are results of continued research and responsible management, and demonstrate the pioneering instinct of American industry. The three producers in New Mexico and the producer in California received the Army and Navy E award for their excellent production records during World War II.

In 1947, the equivalent of 1,029,875 tons of potash was produced from the three mines in New Mexico, brines in California, Michigan, and Utah, and cement dust in Maryland. Exports to 28 foreign countries totaled 68,102 tons, of which 57,337 tons was for agricultural use and 10,765 tons for chemical purposes.

In order to compete with high-grade domestic muriate, imports of potash for agricultural use have improved in grade. Imports of kainite (14 to 20 pct potash) dropped from a high of 640,042 tons in 1910 to 36,175 tons in 1940, and manure salts from a high of 453,242 tons in 1928 to 442 tons in 1940. Imported muriate reached a peak of 306,047 tons in 1930 as compared with 152,494 tons in 1940. In the latter year, 3449 tons of potash valued at \$2,411,919 was imported for chemical uses, 2381 tons of bitartrate (argols), 664 tons of carbonate, and 404 tons of miscellaneous potash materials.²⁴

World

Alunite was mined in Italy for the production of alum as early as 1816.⁴ Soluble salts were first produced in Germany in 1861. In Poland, potash salts were noted at Kalsz in 1854 but only since 1920 has production been continuous. The first production of soluble salts in Alsace was in 1910, in Spain in 1925, in Russia in 1930, and in the United States in 1931. Production from brines was started in the United States and Ethiopia in 1915 and in Palestine in 1930.

Statistics on world deliveries of pure potash during the war are not available but the latest information indicates a production in 1946 of about 3,500,000 tons, about one fourth of which was produced in the United States.

In recent years about 90 pct of the total potash production has been used in fertilizers. Prior to 1890, however, the consumption of potash in Germany by industry exceeded the consumption by agriculture.

SEARCH FOR POTASH

The potash salts of commerce occur largely in deeply bedded saline deposits. Such deposits are discovered in the course of mining salt or drilling for salt, oil, or water. After the presence of potash has been determined, core-drill tests are made to determine the extent and value of the deposit.

In Germany one core test at least was considered necessary before sinking a shaft. In Alsace the entire deposit was well defined during the early stages of development by drilling 165 core tests.

Early explorations in the United States were made by Government agencies and private enterprise of ancient lake brines and salt deposits in western areas; for instance, ancient Lake Bonneville, of which Salt Lake, Utah, is a remnant; ancient Lake Lahontan, of which Pyramid Lake, Nevada, is a remnant; the Owens Valley region, California, containing Searles Lake; the Salton Sea area in southern California, which was cut off from the Gulf of California by the delta of the Colorado River; and the Permian Basin of New Mexico and Texas. Investigations were made also of the shallow lake regions of western Nebraska and of the eastern salt deposits, including salt beds cut in drilling for oil. Still other investigations were made of rocks containing potash—feldspar, alunite, greensands, leucite, and shales—of the dust from cement and blast-furnace operations, and of organic substances.

The sequence of events leading to the discovery and development of the potash deposits in the Permian salt beds in New Mexico was somewhat as follows:³³

In 1911, Phalen²⁶ pointed out that the red beds of the southwestern part of the United States contained deposits of gypsum and salt and were possible sources of potash salts. In 1912, J. A. Udden, then director of the Texas Bureau of Economic Geology, found potash in the brine of the Spurr well, drilled for water, in Dickens County, Texas.⁴⁴ In 1915, he found some red salts with 9.2 pct K_2O , in the Boden well in Potter County, and some red crystals with 6.1 pct and clear crystals with 10.5 pct K_2O in the Miller well, Randall County. However, the potash minerals were not identified.

In 1917, two wells were drilled specifically for potash in the Permian Basin—one churn-drilled by the United States Geological Survey at Cliffside, Potter County, Texas, between the Boden and Miller wells, in the area that had shown, from chemical analyses of oil-well cuttings, the most promising potash possibilities; and the other a core test drilled by E. J. Longyear near Carlsbad, New Mexico, about 15 miles west of

the present developed area. Neither of these wells revealed any notable amount of potash.

Chemical examinations of cuttings from some wells drilled for oil in the Permian Basin were made during the war period but not until 1921 was any potash mineral from that area definitely identified.

Polyhalite was the first potash mineral from the Permian Basin to be identified. Identification was made by R. K. Bailey in the laboratory of the United States Geological Survey early in 1921, in cuttings from the Bryant well, Midland County, Texas, and, at about the same time, in cuttings from the Burns well, Dawson County, Texas. Two specimens, weighing about one ounce each, were found in cuttings from the Pitts Oil Company's well in Ward County in the same year. The Means well, in Loving County, was the first from which samples of cuttings were taken at 5 to 10-ft intervals and carefully analyzed. In 1926, that well was offset by the Eldridge core test, which disclosed the presence of several polyhalite beds.

In 1925, samples of cuttings were selected by V. H. McNutt²³ from several horizons in the Snowden-McSweeney-McNutt No. 1 oil test drilled in Eddy County, New Mexico. A portion of the cuttings was examined petrographically in the United States Geological Survey laboratory by R. K. Bailey, who identified the mineral sylvite in the 1302-ft zone, which, by chemical analysis, in terms of K_2O contained only 3.09 pct. The Snowden-McSweeney Co. was sufficiently interested in the discovery of even that small percentage of sylvite to drill a core test near by and sylvite equal in richness to some of the European crude salts was discovered. Further prospecting in that locality led to the development of the first potash mine in New Mexico.

The first natural sylvite found in the United States was from a depth of 4800 ft in the Gray No. 1 well, drilled in the Markham Dome, Matagorda County, Texas, and the second from a depth of 3910 ft in the Crescent Eagle well, Grand County, Utah. All three discoveries were made in 1925 but to date only the New Mexico deposit has been developed.

PROSPECTING

Under the act of June 25, 1926,²² sponsored by Senator Sheppard and Representative Hudspeth, both of Texas, drilling for potash in the Permian Basin was pursued by the Government through a cooperative arrangement between the Bureau of Mines and the Geological Survey. During the next 5 years, 23 holes were drilled in the basin, 13 in New Mexico and 10 in Texas.²² In 1944, 16 other core tests were drilled by the Government in New Mexico³⁸ to determine the potash resources in four sections of public land set up by the Government as a reserve. Approximately 300 other core tests have been drilled by

private interests in New Mexico and the Government has examined cuttings from many holes drilled for oil throughout the United States.

From 1934, when action on applications for potash-prospecting permits on public lands was suspended, to 1947, when withdrawn lands in eastern Utah were restored to entry, exploration in the Paradox Basin in that state was confined to the examination of cuttings and cores from holes drilled for oil on Government, State, and fee lands. The results, as given by Dyer,¹⁰ of the examination of cuttings or cores from 11 wells indicate the presence of large reserves in that area. The cores of six other wells have been examined but the results have not been released by the operators.

All core drilling for potash in the salt series of the Permian Basin is done with double core barrels, which permit the inner barrel to remain stationary while the outer barrel rotates. Bits set with bort and diamonds of various types were tried, and those set with diamonds with a sharp cutting edge were found to be more satisfactory than Stellite and other hard-alloy bits. The diameter of the core is $2\frac{1}{2}$ in. and core barrels range from 15 to 20 ft in length.

In normal practice, a hole is churn-drilled to the top of the salt, then cased. The water is cemented off before coring is started in the salt formation. The contract price for coring has ranged from \$4 to \$17 a foot, according to economic conditions, the number of holes to be drilled at a time, the length of moves, the cost of building roads to the location, and the number of feet to be cored in a hole, which has ranged from 100 to 1676 ft.

The solution used in coring soluble formations is important. In the Longyear hole, already mentioned, both oil and brine solutions were tried. In later drilling, when it was found that a saturated salt brine was unsatisfactory, magnesium chloride and potassium chloride were added. A saturated solution of crude brine salts or brine from the refinery circuit supplemented by drilling fluids is now used¹⁵ and a high percentage of core is obtained, with little or no etching of the core by the drilling solution.

In eastern Utah, a rotary oil-well rig with a Reed B-R wire-line core barrel has been used in coring salt formations.³¹ It was first used in 1942 in the so-called Thompson magnesium well, near the Crescent Eagle well, with gratifying results, in coring from a depth of 2105 to 4207 ft. The drilling fluid used in this well consisted of Zeogel, Impermex, magnesium chloride, and common salt. At least six other core tests have since been drilled in the salt formation in Utah with a wire-line core barrel.

Core Sampling

In Europe the general practice in prospecting is to drill cores 5 to 8 in. in diameter, using a single core barrel and a solution saturated

with carnallite. Sampling is done by drilling a hole about $\frac{5}{8}$ in. in diameter through the center of the core. In this way a sample is obtained that is unaffected by the selective dissolving on the outside of the core.

In New Mexico, the sections of core taken from the core barrel are logged, transferred to a portable core box and taken to the laboratory for mineralogic examination and sampling. The entire core is examined mineralogically and samples for analysis are cut from the portions that are of potential economic value or that occur in the same horizons as valuable beds in near-by holes. Sections of the core containing polyhalite or langbeinite are split in half with a regular core splitter. Core containing the softer minerals, sylvite, halite, or carnallite, is cut with an ordinary hand saw or band saw. One half of the sample is preserved for future reference. The other half is split again; one fourth is either ground or a portion is taken for analysis, and the other fourth, if the hole is on Government land, is sent to the Geological Survey for mineralogic and chemical check. In the Geological Survey laboratory, the sample is ground from the center or inside portion with an emery wheel, the amount taken being proportional to the length of each piece of core sampled. A small amount of the ground salt is crushed to a powder, immersed in oil with known index of refraction, and examined mineralogically under a microscope.

MINING METHODS

United States

The first shaft for potash in New Mexico was started near Carlsbad by the United States Potash Co. in December 1929 and completed in January 1931. The company completed its air shaft in 1933. The Potash Company of America sunk its first shaft in 1933 and completed its air shaft in November 1936. The Union Potash and Chemical Co., now the International Minerals and Chemical Corporation, started its first shaft in September 1936 and completed it in January 1940. One bed of langbeinite and one bed of sylvite were developed by its No. 1 shaft. Its No. 2 shaft was started in 1940 and completed in 1941.

In sinking³⁵ shafts, jackhammers with straight cruciform bits and the usual V-type cut of shaft round were first tried. However, it was found that in many of the strata, particularly in clays and sands, the shots would chamber and not break clean. This difficulty was overcome by the use of jackhammers with nonrotating chisel bits, similar to those employed in breaking up street pavements. These bits were entirely satisfactory in soft formations and eliminated the necessity of blasting. The United States Potash Co. made a record of sinking 296 ft and cutting four stations in one month.

In the development of the sylvite bed in the International mine, a

record of 153.3 ft was made on Sept. 18, 1940, in advancing the main north entries. A round was undercut, drilled, and blasted in 70 minutes.¹⁸

Potash salts are mined by the room-and-pillar method used in coal mining. Normally the salts in 50 pct of the area are recovered in the first mining.

Sylvite is hard to break with an advancing face, as the ore is tough and tenacious, though not hard.²⁰ When blasted, it tends to break in slabs rather than in fine pieces, which decreases the mechanical loading efficiency. Breaking the salt into small lumps by using an excess of explosives gives a decided advantage in handling. Langbeinite is more brittle and requires less explosive than sylvite.

As an aid in blasting and loading, all faces are now undercut by the same types of machines used to undercut coal. These machines, with a 9-ft cutter bar, advancing at a speed of 4 to $6\frac{1}{2}$ in. a minute, cut a section at the bottom of the deposit 5 to $5\frac{1}{2}$ in. high. Cutting bits of several types have been tried and hard-surfaced bits are now used. Those pointed with Stellite or other alloy are good for about 80 to 100 lin. ft. In the langbeinite bed, the cutting is done in the underlying salt.

There are several advantages in undercutting,²⁷ such as a saving in the cost and handling of explosives, a smooth surface upon which the mechanical loading and haulage units can operate with greater efficiency, and better control in breaking to the bottom of the deposit without leaving high-grade salts or including salts of no value.

Mounted electric auger drills are used in drilling holes for blasting in the sylvite deposits and air drills are used in the langbeinite deposits. The holes are $1\frac{5}{8}$ to $1\frac{7}{8}$ in. in diameter and have an average depth of $8\frac{1}{2}$ ft. Three to five rows of holes are spaced vertically and 10 to 14 horizontally in a face 10 ft high and 40 ft wide. All shots are fired electrically and few misfires occur.

Modern coal-loading machines of different types are used for loading. The potash salts are transported underground by trolley and storage-battery locomotives with cars of $4\frac{1}{2}$ to $5\frac{1}{2}$ tons capacity and, for trackless haulage, by trolley and storage-battery shuttle cars with a capacity of as much as 12 tons. The rubber-tired, two-wire trolley shuttle cars used in the International mine are said to be the first of that kind to be used in the mining industry. Bulldozers are used to maintain the shuttle-car haulageways and to clean up after loading.

The salts are dumped into skip pockets underground and either are crushed or run over grizzlies, where the large pieces are broken by hand tools. They are then hoisted in skips with double-cylinder drum hoists electrically operated and equipped with electric speed and over-wind controls. The waste salts from mining are used for backfilling.

Ventilation—Analyses of the mine air have shown only traces of methane but precautions are taken against any sudden liberation of flammable gas, such as sometimes occurs in European potash mines. A pocket of gas under high pressure was struck in sinking the first shaft. This gas contained hydrogen, methane, and a high percentage of nitrogen.

Modern electrically operated fans are used. They are housed in steel and concrete structures, so arranged that the air current can be reversed easily and quickly.

Concrete overcasts and undercasts are used to control ventilation. Some stoppings are built with salt moistened with a saturated brine that causes it to become solid without dissolving out the small particles of salt and making it porous.

Europe

Potash-bearing beds in Europe range from relatively flat to highly and complexly folded beds and the method of mining varies with the attitude of the deposit. The method generally employed in mining the steeply dipping deposits in Germany is overhand chamber stoping combined with backfilling. After a stope has been opened, the first slice from the back is drilled and shot progressively over its entire area. Then only sufficient salt is drawn to keep about $6\frac{1}{2}$ ft of head room until a higher crosscut about 30 to 36 ft up is reached. The stope is then emptied of potash salts and filled with waste salt dumped from above. In some cases, the filling is obtained from a stope driven for that purpose, supplemented by waste salt from the refinery, which, being moist, tends to solidify and form a hard mass in the mined-out area. After the stope is filled to within about 6 ft of the top, the same procedure is followed in removing the next higher section. Backfilling is required by law but no definite time is specified for its accomplishment. In the flatter beds, the room-and-pillar method prevails.

In the French mines, where the beds have gentle dips, the potash is mined by a longwall advancing system; lumps of waste salt picked out during the course of mining being used for building pack walls behind which the finer waste salts are shoveled. Where waste salts are not readily available, the pack walls are built at right angles to the face and only half of the area is backfilled.

In Poland, the mined area is backfilled hydraulically with waste salt from the refinery.

PREPARATION FOR MARKET³⁴

The process of refining the crude salts mined in New Mexico differs materially at each plant. In two of the mines, primary crushing is done underground. The mine-run material is taken from the head-frame bins by belt conveyors to crushing-plant bins and thence over

crushers and screens of various types. Some of the screened product is sold to the trade as manure salts containing from about 35 to 48 pct of sylvite (KCl), equivalent to 22 to 30 pct K_2O . In some instances, 60 pct muriate is used to enrich the manure salts to the desired grade.

At the United States Potash Company's refinery, the crude crushed salts are converted by a process of solution and fractional crystallization⁸ to a finished product averaging more than 99 pct KCl . The process is based on the relative solubility of sodium chloride and potassium chloride. When both salts are present in quantities sufficient to allow complete saturation, they are radically different in their response to changes in temperature. Increase in temperature enhances the capacity of mother liquors for potassium chloride but effects little change in their capacity for sodium chloride. A selective extraction of potassium chloride is possible therefore. The process includes extraction, cooling, filtering, and drying. It is cyclical in nature and largely continuous. Heat is introduced into the system by means of heat exchangers fed with cold mother liquors. A coarse, granular product is made by tabling.

The process of fractional crystallization⁸ used in refining crude salts containing sylvite is not new, but improvements in apparatus made available by pioneering American manufacturers of such equipment have advanced the efficiency of the American industry. Alloys of various kinds, concrete, rubber, and wood, are used in appropriate places.

Steam for both power and heating is generated in Stirling boilers by the use of natural gas from eastern New Mexico. Turbogenerators of the Curtis type are used for power, and full use is made of exhaust steam from the turbines for heating. All condensates are returned to the boilers to ensure a suitable boiler-feed water. Electrical energy is generated at 440 volts and is stepped up to 33,000 volts for transmission to the mine, about 16 miles to the north.

At the plant of the Potash Company of America, the crude salts are concentrated by flotation. The separation by flotation of sylvite and halite, which differ only 0.16 in specific gravity, can be accomplished in the laboratory in different ways. Experimental work, initiated in the Geological Survey, on mechanical separation of halite and sylvite led to cooperative experiments of the Bureau of Mines and the Potash Company of America at the Missouri School of Mines, where small-scale tabling tests, using flotation reagents, were made in the production of a granular product for which there was a market demand. The tests were successful but it was decided to experiment further before production on a commercial scale was attempted. Later research by the company's staff on flotation of the fine-mesh salts resulted in the development of the process now used at the company's plant. The adaptation of flotation to soluble salines is an outstanding advance in mineral separation.

In production of the refined product,²⁸ the mill feed from the storage bins goes into four pebble mills with steel liners and two regular ball mills. Brine, saturated with sylvite and halite at room temperature, is added in order to prevent the sylvite from dissolving during grinding. The finely ground product goes into two Akins classifiers in closed circuit with the pebble mills and the fines from the classifiers pass on to a Dorr thickener. From the thickener, the pulp goes to a Minerals Separation Co. rougher flotation machine, where the reagents are added to float the salt (halite) and depress the sylvite. This process can be reversed if desired.

The refined product contains from 96 to 99 pct KCl with a high recovery of the sylvite.

Power is developed by diesel engines supplemented by purchased power. Water used in the power plant and refinery, except that obtained from the shaft, is piped to the mine from Carlsbad. As the salts are not put into solution, relatively little water is used in the process at the mine of the Potash Company of America. An interesting development is the use of the jacket water from the diesel power plant to heat the brine developed in the process. This procedure has a desirable cooling effect on the jacket water and affords a heat transfer.

A coarse, granular product is made by fusing and granulating the refined sylvite and a chemical grade is made by treatment of the brines.

Potassium sulphate and hydrochloric acid are made at hydrochloric acid plants at Fort Worth, Texas, and Tulsa, Oklahoma, in a base exchange of the refined sylvite with sulphuric acid.

The International Minerals and Chemical Corporation separates the sylvite from halite by flotation to produce muriate; makes a coarse, granular product by tabling; removes the halite from the crude langbeinite by washing to make potassium magnesium sulphate, and, by a base exchange of langbeinite with sylvite, converts the magnesium sulphate to potassium sulphate and magnesium chloride.

Production of potash from the brine at Searles Lake at Trona, California, began in 1916. The brine contains many chemical elements, and continuous research is required for improvement in their recovery. Potash, borax, soda ash, salt cake, sodium lithium phosphate, and bromine compounds are recovered. Potassium sulphate is made by a base exchange with sodium sulphate. The phase system on which the success of the operations depends has been described by Teeple⁴⁰ and Gale.¹³

At Wendover, Utah, solar evaporation is used to evaporate the natural brines, which contain about 1.2 pct potassium chloride, 1.6 pct magnesium chloride, and 19 pct sodium chloride. The brines are collected in about 50 miles of canals about 14 ft deep, in an area of about 75 square miles, and the sylvite is separated from the halite by flotation.

These brines occur in the Bonneville Salt Flats, also called the Salduro Marsh or Great Salt Lake desert, and were a source of potash during World War I.⁴³

TESTS AND SPECIFICATIONS

For agricultural use, the composition of the salts appears to be of little concern except for the soluble K_2O content, which is closely checked under the laws of the various states. The official methods of analyses of the Association of Official Agricultural Chemists largely govern the methods used in analyzing potash for agricultural use, and many of the concerns that make potash analyses receive periodic samples for check analyses.

When mixed fertilizers are sold in bags, each bag must be labeled as to its content of the three fertilizer elements—nitrogen, phosphate, and potash—and heavy fines are imposed for misrepresentation. To mix fertilizer materials containing the three fertilizer elements with limestone, dolomite, borax, organic material, and other products requires much skill because of differences in specific gravity, texture, and granulation of the materials going into the mixture.

A purchaser of fertilizer can depend on the percentages of the three elements indicated on the tags but, as the percentages of other constituents are not given, the information is insufficient to indicate the value of the fertilizer to plant production. For instance, as shown by Turrentine,⁴¹ salts marketed as high-grade kainite may not contain any of the mineral kainite, magnesium, or potassium sulphate, but may be composed largely of potassium and sodium chloride with rock salt predominating. In view of the time and expense involved in making tests on plant production, a full disclosure of the constituents of fertilizers should be required and a petrographic and analytical examination of the materials should be published, together with experimental data.

Potassium chloride, with less than 1 pct impurities, is the base used in America for the manufacture of chemicals. The specifications for potassium feldspars used in the ceramic industry are very rigid for elements such as iron, which affect the color, and elements that affect the texture, but for other elements that normally enter the mixture, such as silica or aluminum, considerable leeway is given.

USES

When the early settlers reached America, they found the Indians using wood ashes and fish to fertilize their crops. It is not known when wood ashes were first used as a plant food or as a source of potash for industrial purposes but until sometime after 1869, when mineral potash was experimentally introduced to American agriculturists, wood ashes continued to be the principal source of potash.

Until about 1890, potash was chiefly used in dyeing and tanning and in making glass, pottery, soap, matches, fireworks, and explosives. It is still an essential element in industry but, with the increase in production for agricultural use, now only about 10 pct of the production is used by industry.

Ample potash for plant growth occurs in most soils except very sandy soils, peat, and muck, but much of it occurs with silicates that are not sufficiently soluble to make it available in the quantities required. Although enough potash may become available each year to support a moderate plant growth, particularly if the growth decomposes in place, under intensive cultivation, where a large part of the crop is removed, soluble potash must be added. Leaching, erosion, and intensive cultivation deplete the available potash in the soil, as indicated by the present large demand for potash for use in the rich soils of the upper Mississippi Valley.

Potash aids in the formation and storage in plants of starches and sugars, improves the shape, flavor, color, and shipping and keeping qualities of vegetables and fruits, strengthens cell walls of straw in grains and stalks of plants, and increases resistance to disease and destructive insects.⁴³ The lack of potash during World War I was regarded as the main cause of the bad condition in which fruit and vegetables reached the markets.

As potash deficiency is accompanied by deficiency in other plant foods, it is most effective when used with proper amounts of phosphates, nitrates, and other plant foods, such as calcium, magnesium, sulphur, borax, and other elements.

Potassium is an important element² in the chemical and processing industries as well as in agriculture. KCl, with less than 1 pct impurities, is the basic compound for other potash salts of commerce, of which there are more than 100. A few of these salts, with some of their uses and domestic production where available, in short tons in 1944, are listed in the following paragraphs.

Potassium aluminum sulphate $\text{KAl}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$ made from aluminum sulphate and potassium sulphate, used in dyeing, printing fabrics, purifying water, in the preparation of catalysts in syntheses of ammonia, and in making baking powder. Production 4500 tons.

Potassium bichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), used as an oxidizing agent and in dyeing, tanning leather, electroplating, photography, and in making medicines, poison, flypaper, glues, mirrors, and in electric batteries for depolarizing dry cells and in organic chemistry. Production chromate and bichromate 3665 tons.

Potassium bitartrate ($\text{KH}(\text{C}_4\text{H}_4\text{O}_6)$), derived from wine lees, used in baking powder, tartrates, medicine, and in galvanic tinning of metals. Production estimated 1000 tons.

Potassium bromide (KBr), derived from brine and soluble potash deposits, is used in the drug and chemical industries and especially in lithography. Production 1500 tons.

Potassium carbonate (K_2CO_3), formerly made by the Leblanc process, is now for the most part made by the electrolysis of potassium chloride followed by carbonation, using scrubbed flue gases. It is used in tanning and electroplating and in making other chemical compounds, medicines, textiles, mineral water, and glass, including electronic glassware. Its use in the manufacture of glass is hereinafter given in more detail.

Potassium chlorate ($KClO_3$) is made by subjecting a solution of potassium chloride to the action of a direct current of electricity in an electric cell. It is used as an oxidizing agent and in the manufacture of explosives, percussion caps, fireworks, matches, medicines, black dyes for cotton and wool, and anilin dyes. Its most recent use, developed during World War II, is in jet propulsion. Production 10,000 tons.

Potassium chloride (KCl) is used in industry primarily for making other compounds of potassium. A refined grade for the chemical industry is produced by two potash companies and the agricultural grade of another producer has long been used in industry. About 10 pct of the amount produced is used in industry.

Potassium cyanide (KCN), made from sodium cyanide and well known for its use in leaching gold from ore, is used for heat-treatment of steel, in electroplating, engraving, and lithography, and in making insecticides.

Potassium ferricyanide or red prussiate ($K_3Fe(CN)_6$), made by oxidizing a solution of potassium ferrocyanide (yellow prussiate) with chlorine, is used in coating blueprint paper and in preparing pigments, in tempering iron and steel and in electroplating. Production of ferri-cyanide and ferrocyanide is estimated at 500 tons.

Potassium hydroxide (KOH) is produced by the electrolysis of a potassium chloride solution and usually is shipped as flake, solid caustic, or a concentrated solution. It is very soluble in water, absorbs carbon dioxide readily, and is one of the strongest bases known. It serves as a base for the manufacture of many of the potassium compounds and is used in photoengraving and in making soft soap, paint and varnish removers, aviation gasoline and synthetic rubber, and in treatment of leather and cleaning and refining of metal. Production 22,131 tons.

Potassium iodide (KI) is made by the action of potassium carbonate on ferrous iodide or potassium hydroxide or iodine. It is used in medicine and photography, as a chemical reagent, and in table salt, drinking water, animal and poultry feed.

Potassium nitrate (KNO_3) was referred to by Jeremiah in the seventh century B. C. The crude product is used in fertilizers. The re-

finer product is used for pickling meats, in the manufacture of black powder, fireworks, matches, glass, in tobacco products, and for tempering steel.

Potassium permanganate (KMnO_4) is made by fusing manganese dioxide and potassium hydroxide and oxidizing the product in electrolytic cells to 99 pct pure potassium permanganate. It is used largely as a bleaching agent, as an oxidizer by industry, as an antiseptic in medicine, in purifying water, and in tanning and photography. An important military use is as an ingredient of the filler in gas-mask canisters for the absorption of lethal gases.

Potassium phosphates. The tripotassium phosphate is probably the best known of the potassium phosphates. It is usually made by the reaction of potassium hydroxide with phosphoric acid and is used chiefly as a water-softening reagent and in detergents. The monopotassium and dipotassium phosphates are used in special fertilizers and in the growing of penicillin and similar micro-organisms.

Potassium silicates. The principal source of potassium silicates used in ceramics is the feldspars. Ground feldspar sold by merchant mills amounted to 381,728 tons in 1945, of which 95.6 pct was for use in the ceramic industry. Neither the tonnage of potash contained in the feldspars nor the tonnage of potash feldspars used is available.

Glauconite (greensands) has been used in New Jersey for more than 100 years and considerable research was done during World War I on the extraction of potash therefrom. The employment of greensands as a water softener is closely related to the use of artificial zeolite. In 1946, a total of 5140 tons of refined material, valued at \$424,900, was sold for water softeners.

Silicate is produced from potassium carbonate and silica for use in the manufacture of welding-rod fluxes and is especially valuable for coating rods used in welding by alternate current.

The alkali or soda-potash content of glass varies with the type of glass.³⁹ In thin, blown glass in bulbs it is as much as 20 pct. In several respects, potash improves the quality of glass, but its cost has limited its use in the less expensive articles. The best quality of crystal tableware, with high brilliance and good musical tone, is generally a straight potash-lead-silica glass, with 7 or 8 pct potash. Good chemical durability or resistance of glass to weathering is ascribed to its potash rather than its soda content. Because of the easy reduction of lead oxide in the founding process, potassium nitrate is almost universally used to maintain oxidizing conditions in this type of glass.

In X-ray lead glass, church windows, and sculptured glass, practically all the alkali is potash, as it makes the glass more colorful; also, where durability and color in optical flint glass are desirable, the potash content is customarily about twice the soda content. Potash-silica glass

is not affected appreciably by ultraviolet radiation, whereas soda-lime and silica glass are unstable photochemically. When soda is put in glass for double glazing or for insulation and other uses, a white coating often forms on the interior sides of the plates, but with 6.5 to 10 pct of potash in the mixture, this is avoided. For chemical wares, a potash-soda glass is superior to that type of glass made without potash.

In ordinary enamelware, the potash is normally supplied by feldspar. Enamels of the jewelry type, where high brilliance and luster are desired, are of the potassium-lead-silicate type with as much as 36 pct pure potash. As a fluxing material in glazed ware, potash may be found to be a satisfactory substitute for lead in supplying brilliance and luster.

In making fiber glass for electrical insulation, the value of potash has not been adequately determined, but in a range of temperature from 100° to 400°C, insulation is improved by the use of soda and potash in the ratio of 1 to 4.

PRICE HISTORY

The price of agricultural potash salts increased more than tenfold during World War I, as shown by the following quotations:

In 1913, muriate was quoted at 76¢ a unit,⁴² kainite and manure salts at 68¢. During World War I, the price of potash is said to have reached \$600 a ton. In December 1915, it reached \$9.87 a unit or \$987 a ton of pure potash equivalent in muriate, and \$9.05 a unit or \$905 a ton in sulphate, and it did not drop below \$1 a unit for any grade from March 1915 to April 1921 or for sulphate until October 1921. During this period, the price of manure salts did not exceed \$300 a ton or the price of kainite \$363 a ton. In November 1921, muriate dropped to 74¢ a unit, kainite to 60¢, and manure salts to 55¢, and since that time prices have continued lower than the 1913 prices.

During a part of the season 1934-1935, potash was reported as selling as low as 27¢ a unit on the Atlantic seaboard but the lowest published price was 40¢ for muriate and 43¢ for manure salts, with seasonal discounts as high as 12 pct with a guarantee to protect the buyer if potash was offered at a lower price. The base price of muriate, normally 10¢ a unit above the lower-grade salts, was reduced to 3¢ below.

A comparison of the high prices during World War I with the normal prices during World War II emphasizes the importance to the nation of the discovery and development of the New Mexico deposits.

In 1948, potassium chloride is quoted at 37½¢ per unit of K₂O f.o.b. Carlsbad, New Mexico, manure salts at 20¢, 90 to 95 pct sulphate of potash at \$30 a ton, and sulphate of potassium magnesium at \$14.50 a ton subject to a 12 pct discount for equal monthly delivery throughout the year. The unit price of muriate at Trona, California, is 45.5¢. The cost of transportation from the point of origin to points east of the

Mississippi River ranges from 30 to 50 pct of the delivery price. Potash imported from Europe is reported at 85¢ a unit at Atlantic ports.

Caution is necessary in comparing the price of domestic potash sold for fertilizer in the United States with the price of salts imported and exported because of the difference in the basis of quotations. Quotations on domestic potash salts of agricultural grade, formerly based on prices for the respective grades c.i.f. Atlantic, Gulf, and Pacific ports plus freight to interior delivery points, are now based on the price at point of origin. Quotations on exports include freight to the port of delivery and, in some instances, freight to destination.

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CHAPTER 35

PRECIOUS STONES

BY SYDNEY H. BALL*

MINERALS used primarily for personal adornment and decorative purposes are called precious stones. To be so prized, the stones must possess beauty of color, must not be too common, and must be hard enough to withstand ordinary wear. If transparent, they must have brilliancy and fire. Almost one hundred minerals have been used as precious stones, the noble gems being the diamond, emerald, ruby, and sapphire; pearls are frequently included by courtesy. These gem stones, however, are sometimes equaled in beauty by fine opals, aquamarines, tourmalines, spinels, chrysoberyls (both cat's-eye and alexandrite), and spodumenes (hiddenite and kunzite).

The Greeks, Romans, and medieval Europeans grouped together gem stones according to color and degree of transparency, and only as the niceties of mineralogy began to be known, about a century ago, was it realized how many different minerals have the beauty required of gem stones. Pliny, for example, did not distinguish between rubies and the red varieties of spinel and garnet, although he conjectured that the beryl and emerald were one mineral.

GENERAL SURVEY

Early man treasured bright colored berries, attractive shells, white teeth of wild animals and brightly colored pebbles, and used them as personal ornaments.

In the eastern hemisphere, the earliest stones used were members of the quartz family (100,000 to 75,000 B.C.); then obsidian and amber (50,000 to 25,000 B.C.); the jade minerals, fluorspar and jet (22,000 to 7000 B.C.); turquoise (7000 to 3400 B.C.); lapis lazuli and garnet (prior to 3500 B.C.); emerald (2000 to 1800 B.C.); sapphire, ruby and diamond (800 to 500 B.C.). Indeed, gem mining is the oldest form of mining, and before any metals were known primitive man recognized about 18 gems and decorative stones. At first he sought them in stream gravels and residual deposits but by 3400 B.C. the turquoise mines of the Sinai Peninsula were operated. This was the world's first important hard-rock mining enterprise. The Afghanistan lapis lazuli mines may

* Rogers, Mayer and Ball, New York, N. Y.

be almost as old. The emerald mines of the Egyptian Red Sea coast were operated at least as early as 1925 B.C., and the olivine mine of Zebirget Island, Red Sea, was opened between 1580 and 1350 B.C. It is believed that the diamond deposits of India and the sapphire-ruby mines of Ceylon were producing as early as 800 to 600 B.C. The mines of amber in Prussia were the most important from some time prior to 7000 B.C., then the center of production moved to the borders of the Red Sea, from which in about 200 B.C. it was transferred to India and Ceylon. First place was usurped in 1725 A.D. by Brazil, which in turn was superseded by South Africa in 1870. Similarly, the center of the world's trade in gems has been successively Babylon, Alexandria, Rome, Venice, Amsterdam, and now London, Paris, Antwerp, Amsterdam, Bombay, and New York.

When the white man first appeared on our shores, the American Indian was using more precious and decorative stones than were the people of the eastern hemisphere. He depended mainly on gravels for his gems but his underground operations for turquoise and obsidian were large. He also mined emerald, quartz, and many decorative stones. The trade in gems was wide; that in New Mexican turquoise extended from Yucatan to Wisconsin, and the stocks of Colombian emeralds in the hands of the Peruvian Indians were so large that for at least 200 years after the Conquest the gem was known as "Peruvian emerald." The Indians used jasper and chalcedony as early as 15,000 B.C., and agate, jade, jet, obsidian, turquoise and a host of other minerals were used before the beginning of our era. Amber, emerald, garnet, lapis lazuli, sodalite, variscite and opal were mined before 1000 A.D.

USES

By far the largest part of the world's gem production is used for decorative purposes, mainly in jewelry but to a lesser extent as material for statuettes, vases, and other objets d'art. For the latter, the less valuable gem stones are usually employed, although statuettes of sapphire and ruby exist. The lapidaries of China, Delhi (India) and the Urals are particularly clever in this branch of the art.

To the man of the Stone Age, minerals served not only, as they do for us today, certain purposes but as well those for which we use metals. The worker in stone was the research man, the engineer and the artisan of that day. From agate and flint, the armament worker of the day fabricated spear points and arrowheads. Prior to 3400 B.C., the lapidary shaped seals from hard stones, often gems. Thereafter lenticular masses of rock crystal were cut, possibly for reading glasses. Almost 3000 years before Christ, the Egyptians had a drill that cut annular holes, the predecessor of our diamond drill, although the abrasive was not diamond dust. Greek and Roman gem engravers used the lima, a file of emery

powder embedded in resin: from this his Hindoo confrere may have obtained the idea of embedding gem dust in shellac. Using the same idea today, we bond diamond dust in powdered metal, a plastic or a ceramic and from such material make many useful tools. Prior to the beginning of our era, splinters of diamonds were used in gem engraving, agate mortars and pestles were used by druggists, gem sands fed on wires cut marble into slabs and rock crystal was an ingredient of some glass. The diamond die perhaps stems from the pierced diamonds of Middle Age necklaces.

The diamond is the most important of the gems industrially, its value depending upon its hardness, which is much greater than that of any other substance, natural or artificial. Sir David Brewster, one of England's greatest scientists, prophetically wrote in 1835: "Had the diamond not been placed at the head of the mineral kingdom from its unrivaled lustre and high value as an ornamental gem, it would have obtained the same distinction from its great utility in the arts." Today some 25 pct of the world's diamond production by value (about 80 pct by weight) is used in industry. The revolutionary increase in the sales of industrials was summarized by my friend A. Tremoyne, "from jewels to tools." As opposed to the gem variety, the industrial diamond is ground to powder eventually and is used up. The use of the industrial diamond, long the Cinderella of its socially registered and socialite sister, did not increase much for 100 years after Brewster's day but in the past 12 years it has increased by leaps and bounds, in part because of the wider use of hard alloy steels. Imports of industrial diamonds to the United States did not surpass a value of \$1,000,000 until 1923. Imports of certain typical years since then are given in Table 1.

TABLE 1—*Imports of Industrial Diamonds, United States*

Year	Carats	Value	Value per Carat
1935	954,589	\$4,293,611	\$4.50
1939	3,568,730	9,725,683	2.73
1943	12,172,679	21,938,368	1.80
1946	4,625,282	14,297,536	3.09
1947	4,035,004	13,061,443	3.24

The large consumption in 1943 was due to the many functions performed by the diamond in overhauls in the munition plants. During some of the war years, consumption was double world production, and stocks, the accumulation of years of mining, were badly depleted. Indeed, as early as 1934, stocks of certain types of stones were exhausted and we had to depend on current production.

There are three types of industrial diamonds: (1) bort, a trade name for diamond crystals too badly flawed or too off-color to be used

in jewelry; (2) carbonado or black diamond, a closely knit aggregate of excessively small diamond crystals; and (3) ballas, a globular mass of diamond crystals radiating from a common center. Bort has the virtue of hardness and comparative cheapness, carbonado of extreme toughness, and ballas of hardness and toughness. Bort is a by-product of all diamond mining and makes up about 80 pct of a normal year's production. Carbonado comes from Bahia, Brazil, and ballas from Brazil and certain of the South African mines, notably New Jagersfontein and some alluvial deposits. Bort is relatively abundant, some 6,000,000 to 8,000,000 carats* being produced annually, much of it in the Belgian Congo. Bahia now produces from 20,000 to 30,000 carats of carbonado and ballas is only one fifth as common. Carbonado occurs in pebbles of larger average size than the gem stone, although the largest ever found (3078 carats) only approached in size the famous Cullinan diamond. Bort of good quality but small size retails for about \$7.50 per carat; carbonado is from five to ten times as expensive and ballas may cost twice as much as carbonado. About 1929, the price of the latter was forced to exorbitant heights (\$175 a carat) and industrialists substituted bort for carbonado for many purposes, so that the latter has permanently lost many markets.

Of the multitudinous uses of the industrial diamond, some, like the use of splinters in gem engraving, date from Greek and Roman days, and new uses for the diamond will be found for a long time to come. Incidentally, perhaps its earliest function in America, well over 100 years ago, was to furrow grist-mill stones that had been worn smooth.

A small weight of industrial diamonds in industry performs wonders, as is evidenced by the fact that some are said to have been smuggled out of Great Britain to Germany during the war by carrier pigeon.

As to price—bort is the cheapest; crushing bort but some \$2 a carat (say \$306 a troy ounce); small, good-quality bort from \$5 to \$10 a carat. Carbonado and ballas, according to size, are respectively \$20 to \$80 and \$20 to \$100 a carat.

Industrial diamonds are among the strategic minerals that are to be stock-piled under Public No. 520, 79th Congress.

Diamond tools, first used in 1779, consist of a steel arm in which is set either a rough diamond or one especially shaped for the intended purpose. Sometimes two or more stones are set in a single tool. The diamond must be set in correct relation to its crystallographic axis, to ensure maximum usefulness. These tools are used to shape steel, to sharpen hard-alloy steel tools, to true abrasive wheels, to give a high

* For centuries the carat has been the unit by which most gems are weighed. At one time each gem center had its own carat but now it is almost universally equivalent to 0.2 gram, or 3.086 grains (155.54 carats pertroy ounce).

finish to crankshafts and other aircraft parts, and in countless other ways. The fine tolerances, which permit interchangeability of parts of a thousand airplane engines of the same model, are obtainable only with a diamond-pointed tool, nor without its grinding could engines be driven at their present speed. Billiard balls, ceramics, plastics, felt rolls and vulcanite mouth pieces also are shaped with diamond-set tools.

We are all familiar with the diamond drill, the rifle with which we hunt and get ore bodies. While the drill was a Swiss invention of some 80 years ago, American engineers in the seventies of the last century first applied it to mining. Many of the improvements in both drill and bits have also been made by American engineers.

The cutting agent originally was carbonado, but by 1935 small borts replaced the larger and more costly stones, reducing drilling costs by 50 pct and doubling the daily footage. The diamonds originally were set by hand but now are mechanically set. The old-type bit might cost \$5000; its modern successor as little as \$50. Certain special bits, including some used in blasthole drilling, contain as many as 2000 diamonds, a useful if not particularly beautiful crown.

The deepest diamond-drill hole ever drilled—in South Africa—is a little over 2 miles (10,715 ft) long.

While blasthole drilling started in the Lake Superior iron-ore mines some 35 years ago, modern practice dates from its introduction at Noranda in 1935. At present, some 45 of the larger underground mines on the North American continent are using this cheap and safe method of breaking ore. Much experimentation is being carried on in drifting with either bort-set bits or bits impregnated with diamond dust. The suppression of dust, provided the method can be commercialized, will render underground mining not only less hazardous but also pleasanter.

While the drill is typically a tool of the mining engineer, it is also widely used by the civil engineer in testing dam sites and in locating tunnels, to cite but two examples. In oil exploration, the diamond drill was once widely used in confirming the presence of suspected favorable structures but in this field geophysical surveys have largely supplanted the drill. A generation ago, some Mexican producers were brought in with the diamond drill and within the last year or two wells have been brought in with the diamond drill in both Colorado and Texas. The method has obvious advantages where the rocks are hard and its use presumably will increase.

Some 80 pct of crushing bort is made into diamond-impregnated wheels used in accurate grinding and precise tooling. They are the most satisfactory tools to shape, sharpen and hone cemented carbide tools. Wheels were introduced to the trade in 1933 and between 1936 and 1942 their consumption increased more than fiftyfold. The wheels are now made in shapes and sizes suitable for every type of grinding; for

instance, the tiny ball-bearing races used in precision instruments are given a finish grinding with a special wheel and glass lenses are ground en masse with other wheels. In the manufacture of wheels today the diamond is crushed and the resulting dust is carefully sized for the special use in view. The diamond dust is then evenly mixed with the bonding material, either a plastic, powdered metal, or a ceramic. The mixture is then subjected to high pressure and sintered, the temperature not being high enough to injure the diamond. The bonded material is then mounted as a thin facing to a metal pre-form wheel of the required size and shape. Wheels range in diameter from $\frac{1}{8}$ in. to 20 in.

Diamond dust as such is used wherever a powerful abrasive is needed. It is used in cutting diamonds and the other harder precious stones, also quartz plates for radio. It is used also in shaping diamond dies and watch and instrument jewels and in piercing them.

Crude metal dies for wire drawing date from at least the third century of our era. Diamond dies were first made in 1819 but it was only 50 years later that even the more progressive of the Italian and French drawers of gold wire, to be woven into fine textiles, employed them. The extraordinary growth of the electric lamp industry 60 years ago put diamond dies on the map and they are used today to produce most wire less than 0.08 in. in diameter. While there were a few diemakers in America before the war, it was then essentially a nonmechanized, family and cottage industry centering at Trevaux, near Lyons, France. Through dire necessity during the war, we fostered an important industry and both the United States and Great Britain by 1943 were producing the dies needed, even in the smaller sizes. The process was mechanized and equipment was built producing a number of dies simultaneously. The diamond, a sound crystal of $\frac{1}{4}$ to $\frac{1}{8}$ carat, is first mounted in a metal container after the top and bottom of the stone are ground parallel. Then by hand or by machine the hole is drilled by a needle moistened with olive oil loaded with diamond dust. The hole from one side is funnel-shaped, from the other bell-shaped. The aperture is then carefully polished to an amazing smoothness, diamond dust being again used. The die is now in instances pierced by an electric spark shot from a platinum needle, both needle and diamond being immersed in a chemical.

The object of all artisans is to make a die with the smallest possible aperture (0.0003 in. or less in diameter) the kind our fellow member, Prof. E. H. Kraus, so aptly described as "putting a wire you cannot see through a hole that is not there." But even the best artisans frequently fail to make the holes drilled from the two sides center exactly and the die must be reamed out to the smallest size conditions permit. In the process of making fine wire for lamps or for the instruments on the panel of an airplane, the metal is successively drawn through a set

of dies, each with a smaller aperture. The diameter of the resultant wire is frequently but a fraction of that of a human hair. Lead of the better pencils is once again extruded through a diamond die and the gut leader of a fine fishing outfit is drawn through a diamond die. One of the earlier industrial uses of the diamond, dating in Europe at least to the fourteenth century, is the glazier's diamond, a small octahedral crystal. Such stones are also used to cut the edges and ends of plate glass.

Diamond-set saws, both circular and chain, are used in shaping building stone.

Splinters of diamonds, in addition to their use by gem engravers, are used in engraving lithographer's stones, copper and other metal plates and glass and plastic sheets. They are also used in piercing watch jewels and are mounted in instruments to test hardness. Splinters and other small diamond tools are used by dentists.

In September 1947, the National Bureau of Standards announced that diamonds can replace the Geiger-Müller counter in detecting and "counting" radiations of uranium and other radioactive substances. The counter involving the use of the diamond not only has a longer life than the counter now in use, but, owing to its small size, it is suitable for internal surgery. Thus we have a new warning instrument to protect the lives of atomic workers.

Watch and chronometer jewels and bearings for meters and scientific instruments are made from gems. They are used also in timing instruments, such as mechanical fuses for bombs, switches and microgears. To be satisfactory, the raw material must be both hard and non-brittle. While diamonds, garnets, chrysoberyls, spinels, zircons, topazes, rock crystal and agates have been and are to a small extent still used, the most widely employed materials are the corundum gems, sapphire and ruby. At one time natural gems from Australia and Montana monopolized the market, but they have been largely supplanted by synthetic corundum, which not only is cheaper but is more readily fashioned. Before World War II, all synthetics came from Germany, Switzerland and France; during the war, however, several American firms produced excellent synthetics and other firms fabricated bearings. At present we are self-sufficient as to bearings. The raw material is first shaped into "bolts" by diamond wheels; these are then cut to the appropriate size, then ground to almost paper thinness, and then rounded. Some bearings are not pierced but most of them are, this being done with a mild-steel needle fed with olive oil weighted with diamond dust. Sapphire and ruby, largely synthetic, also are used as needle points for phonographs and dictating machines, as "windows" of combustion chambers, as gauges and as dies. They are also used as abrasives.

The industrial uses of rock crystal, the best of which comes from Brazil, are as diversified as those of the diamond. It is chemically resist-

ant, has a high fusion point, withstands sudden temperature changes, resolves the shorter light-wave lengths and, under piezoelectric pressure, its plates, depending on thickness, vibrate from thousands to millions of times per second. Frequency control in radio and telephone is due to such plates—using quartz plates of different sizes and thicknesses, a plane pilot need only turn a switch to get off one station and into communication with another. With such plates, ships know the depth of water below the keel or the proximity of icebergs, rocks or submarines. Quartz-plate resonators at terminals of oceanic cables or local or long-distance telephone lines divide the range frequencies, permitting many conversations over one and the same wire. Quartz lenses, wedges and prisms are used in microscopes, saccharimeters, spectrographs, spectrometers and monochromators. In the sugar industry, the rotary power of the wedges compensates that of the sugar solution.

Fused quartz or quartz glass is used for flasks, dishes and tubes in the chemical laboratory and for tubes and lamps in the electrical industry, because of its great resistance to temperature changes and to strong chemicals. Quartz fibers are used as highly sensitive springs in precision measurements. At one time the filament of fused quartz (but 0.006 in. in diameter) was drawn by being attached to an arrow shot into a fixed target.

Windows of fused rock crystal are installed in sanatoria because of the supposed curative value of the ultraviolet ray which passes through it. Fused-quartz lamps permit various rays to pass through. The lamps in some mine change houses produce infrared rays, theoretically, at least, giving the men their equivalent of sunshine. In hospitals, the newborn babes are branded on their backs by the rays of a quartz lamp—the branded name or identification number, good for six months, prevents the young hopefuls from being shuffled.

Master gauge blocks and balance weights where extreme accuracy is required are made of rock crystal.

Fluorspar, while to a small extent used in jewelry and to a greater extent in objet d'arts, is, of course, mainly used as a flux in iron furnaces, to produce hydrofluoric acid (and its important derivatives like freon, used in the aerosol insecticide bomb and air conditioning) and as an ingredient of certain glasses and ceramics. A little flawless and colorless fluorite is cut into lenses introduced into lens systems to correct spherical and chromatic errors in microscopes, telescopes and spectroscopes. Prisms of it form essential parts of optical instruments when transparency to the ultraviolet and infrared parts of the spectrum is essential. Our southern Illinois-Kentucky fluorspar district produces some optical fluorspar but most of it is imported from Switzerland, Japan, and Siberia. Synthetic lithium fluoride crystals are said to be a satisfactory substitute.

It is perhaps a slight stretch of the imagination to include calcite among precious stones, although the fibrous variety, satin spar, makes attractive beads for necklaces. From clear pieces of it, the well-known nicol prism, an essential of many optical instruments, is cut. During the war, it was used in a special type of bombsight.

Tourmaline, because of its strong absorption of light when cut into plates perpendicular to the optic axis, is used in tourmaline tongues, a simple form of polariscope. Like quartz, it is piezoelectric but because of its rarity is seldom used.

Because of their hardness, gems are used as abrasives. In addition to the king of abrasives—the diamond—ruby and sapphire, garnet and quartz and to a lesser extent topaz are used as abrasives. All these minerals fracture into sharp-angled fragments. Abrasives may be used as powder or cemented to paper or as an impregnation of one form or another of a matrix. Synthetic corundum tends more and more to supplant the natural stone.

Only about one fifth of the world's amber production is used ornamentally. The rest is distilled at a temperature of 375°C, the by-products being a resin (amber colophony), oil of amber (the *oleum succini* of the druggist), and succinic acid. Before World War II, these substances were very important to the German dye industry. From the days of the early Flemish painters, the varnish has been used on paintings, and *oleum succini*, certainly made prior to 1548, is today used to relieve inflammation and as an antispasmodic.

Agate is made into mortar and pestles, burnishers, knife edges for balances, extremely accurate weights, rollers used in the textile industry and spatulas used in mixing corrosive substances. The "cannic" marble of our youth was also of agate.

Ultramarine, the blue paint of all fine old pictures, was made from lapis lazuli but about 125 years ago it was superseded by a synthetic product. Azurite, malachite and mariposite have from time to time been used as pigments. The ancient Egyptian woman of fashion painted her eyes with malachite powder.

Beryl is the principal ore of beryllium, zircon one of the principal ores of zirconium, and spodumene the chief source of lithium salts. Beryl is used in some ceramic mixes.

Sillimanite, andalusite, cyanite and dumortierite are used for spark plugs and other refractory materials. Zircon, olivine and topaz also are used as refractories.

The Chinese make chimes from plaques of jade.

In the Middle Ages particularly, gems were sovereign remedies, the gem being applied to the affected part or the powder taken internally. Certain Americans still buy amber-bead necklaces to ward off tonsillitis and other affections of the throat.

Precious stones are among the most valuable of commodities and

over a period of years their price trend has been upward. Great wealth is concentrated in them in small compass. They also enjoy an international market. In the Orient and particularly in India, where bank stocks and bonds are unknown to the majority of people, precious stones have been a popular form of investment for centuries. In consequence, the family fortunes of the astute Hindus have from generation to generation enjoyed a reasonable growth. In the West, gems assume the role of concentrated wealth readily hidden or easily transported when people doubt the stability of their country's currency or when political upheavals or religious persecution cause them to leave their homeland overnight.

Precious stones have been a potent factor in furthering exploration. In the Middle Ages, much of Europe's knowledge of the Eastern countries was due to the travels of gem merchants. It was the precious stones of Cipangu (Japan), together with its wealth in precious metals, that lured Columbus to explore for a westward route. In the early exploration of America, similar lure led Europeans forward, although Colombia alone with its emeralds adequately fulfilled their hopes.

GEOGRAPHIC DISTRIBUTION

Precious stones are widely distributed over the world, and while important commercial deposits are few, Africa, Asia, South America and Europe all have deposits of the first rank, North America and Australia alone being without them. Africa, because of its preeminence as a diamond producer, is the most important factor in the industry. Burma, Siam, Ceylon, the Urals, Madagascar, Brazil and southern California are notable for the wide variety of precious stones they produce.

American Gem-stone Deposits

The United States, in comparison with its wealth in most other mineral resources, is poor in precious stones, having no deposit of the first rank. The precious stones sold at many resorts as "local" products are likely to be South American stones cut in Europe and mounted in Providence, Rhode Island. In the past decade, however, there has sprung up in the northwest a relatively important lapidary industry; in part professional, in part amateur hobbyists who specialize in cutting the agates of the region.

However, few countries have produced such a variety of precious stones as the United States, well over 60 distinct species. Adequate statistics as to gem products do not exist but our country since 1880 has produced gem stones to the value of some \$12,000,000. Montana, California, and Nevada have been the most important sources. Sapphire, turquoise and the agate family are the major products, followed by tourmaline, garnet, variscite, and beryl.

While the Mount Mica tourmaline deposit in Maine has been worked

in a desultory manner since its discovery in 1820, the first American gem-mining company was the Emerald and Hiddenite Mining Co., which from 1880 to 1888 operated the deposit at Stony Point, North Carolina. Since the nineties of the last century, supplementing the primitive but age-old mining of the Pueblo and Navajo Indians, the white man has mined turquoise, notably in New Mexico, Nevada, Arizona, and Colorado. The agatized wood of Arizona 50 years ago was cut on a considerable scale; the beauty of the Petrified Forest was threatened but happily the menace disappeared when the area became a National Park.

Sapphires were first found in Montana in the placer mines of the Missouri River in 1865. From the early eighties of the past century to 1944, the gem was an important by-product of dredging or other forms of placer mining. In the nineties the gem was found as a component of a basic igneous dike and from 1896 to 1929 an English company worked the deposit. Montana produces some very attractive, brilliant but rather pale gem stones but most of the production was sold as industrials. With the wartime birth of an American synthetic industry, the Montana sapphire lost its major market. In 1906, diamonds were found near Murfreesboro, Arkansas, in a kimberlite pipe of the South African type. While some 10,000 carats of diamonds have been recovered, no one of the numerous companies that has attempted to exploit the deposit has been successful.

As to jade, nephrite was found in southern Monterey County, California, some 8 years ago but the product of the two more important deposits—of Lander, Wyoming, and of the Kobuk River, Alaska—were first marketed, respectively, in 1940 and 1945. The latter locality has been worked by the Eskimos at least 350 years ago. In both districts the jade occurs in place as well as in alluvial and detrital deposits. The stone is in part cut locally and in part exported to China.

Mesa Grande, San Diego County, California, has produced much beautiful tourmaline of various colors. A considerable quantity of the pink has been exported to China. Kunzite is obtained in the same district. The Virgin Valley, Nevada, has produced some fine black opals and Latah County, Idaho, some attractive white ones. The moss agates of Montana and Wyoming are as fine as any in the world. Lapis lazuli occurs on Italian Mountain, Gunnison County, Colorado. A number of other precious stones appear on the American market from time to time, notably aquamarine and golden beryl, fine amazonstone and splendid malachite and azurite. The ornamental use of gold quartz began in California more than 90 years ago. The deep blue benitoite (California); the yellowish green variscite (Utah) and the rose red rhodolite (North Carolina) are found only in the United States and the world's finest hiddenite comes from North Carolina.

GEOLOGIC OCCURRENCE

Gems occur in practically all types of rocks, in gravel, in veins, and in deposits formed by cold circulating waters and those of descending oxidizing waters. Fossil vegetable matter is represented by amber and jet and fossil animal matter by bone turquoise.

Because of the preponderant position in former times of the South African kimberlite pipes as diamond producers, the basic igneous intrusive rocks were from 1878 to 1921 the dominant original source of gem stones. Sapphire and pyrope also occur in such rocks and if diamond placers are exhausted they may regain the first place. Potash-rich or soda-lithia-rich pegmatites are the source of a bewildering array of beautiful gems, although their combined value has been but one per cent of that of the gems obtained from the basic igneous intrusives. Burmese jadeite occurs as one of a series of soda-rich intrusives. Basic lava flows, granites and andesites furnish a few gems. The metamorphic rocks are relatively unimportant but of them contact-metamorphosed limestone (lapis lazuli and ruby) is the most important, and regionally metamorphosed schists and gneisses (nephrite, etc.) come next. Opals usually are deposited by volcanic waters from acid flow rocks and agate by volcanic waters from basic flow rocks, the former in point of annual value being the more important. Amethyst, rock crystal and gold quartz are the principal gems in veins of magmatic origin and turquoise is the principal gem of supergene origin.

Most gems are heavy, physically resistant and chemically inert, and in consequence virtually all gems occur in stream gravels. Indeed, prior to the discovery of the South African kimberlite pipes, stream gravels were responsible for 95 pct of the world's gems. Many gravel deposits, through concentration and reconcentration of their precious-mineral content, are profitable to work, although the source rock may be relatively poor in gems. Even the excessively hard diamond may have been subjected to such long erosion that it is well rounded. Fractured and imperfect stones cannot endure nature's long milling and in consequence stream gems on the average are of better quality than mine stones. Desert gravels (some diamonds and olivines) are much more important than beach gravels. Amber and jet occur in relatively young sandstones and conglomerates in places contain a few gems.

Rock weathering is important in gem mining, largely because it lessens mining costs and the danger of injuring the gem in removing it. In the weathered zone, the worthless satellites may be dissolved out or removed by wind or water. The weathered "yellow" ground of the South African mines contained in instances six or seven times the diamond content of the fresh pipe rock in depth. Many a gem mine in pegmatite is profitable only in the weathered zone.

POLITICAL AND COMMERCIAL CONTROL

The British Empire, largely because of the diamond production of South Africa, Southwest Africa, the Gold Coast, Tanganyika Territory and Sierra Leone, accounts for from two thirds to four fifths of the value of the world's gem production. The Belgian Congo and Angola, because of their diamond production, account respectively for about one seventh and one twelfth. Brazil produces about 3 pct. The minor producers, each accounting for less than 1 pct of the total, rank as follows: Germany (amber), Siam (sapphire, ruby and spinel), Colombia (emerald), and Ceylon and Russia (a wide assortment of gems). Most of the gem fields are nationally owned but Americans are interested in certain of the diamond mines of the Belgian Congo and Angola. South African pipe mines have always been favorites on the Paris Bourse.

PRODUCTION, CONSUMPTION AND MARKETING

Precious stones are indestructible and virtually all the gems that have ever been mined exist today. Many an Egyptian or Roman gem is worn today by an American woman or a Wall Street tycoon. Of course, in cutting all jewels are reduced in weight, which for diamonds amounts to about half that of the rough stone. Some gems have been lost in shipwrecks, a few have been beaten to powder in a fit of anger (i.e., the Pigott diamond by Ali Pasha), and many have been buried, but enterprising archeologists recover some of the latter and permit us to study them. Gems used industrially are largely destroyed. I estimate that the world's stock of gems, largely in India, the United States and England, is worth nearly twelve billion dollars.

The graph of gem production from 1780 (Fig 1) portrays the remarkable growth of the industry, and indeed that of gem consumption, for the two are practically equivalent. In the eighteenth century the production was stabilized at from \$3,500,000 to \$5,000,000 a year; it then gradually rose to \$8,000,000 by 1871, after which the increased output of the African diamond mines caused a precipitate rise to a peak production of \$97,000,000 in 1928, with deep canyons signaling the World Wars, the 1921-1922 postwar depression, and the depression of the late twenties. At present a normal year's production is about 22 times that of 1700, about 12 times that of 1850, and three or four times that of 1900. The world's diamond mines now produce in a day as many carats as did those of 1700 in a month, but rapid as has been the growth of the industry, its expansion is relatively small compared with the increase of the production of gold and of the base metals. In 1700, diamonds accounted for about half of the yearly production of gems but the popularity of that gem has so increased that it now represents about 95 pct of the total. The increase noted is therefore largely one in diamond output.

It seems probable that alluvial mines were worked by Paleolithic man, and the production from alluvial mines was predominant to 1878 A.D., although from 3500 to 600 B.C. there were doubtless years in which the production of the Sinai turquoise, Afghanistan lapis lazuli and Egyptian emerald exceeded in value the production of gem placers. From 1878 to 1921, the large diamond output of the South African pipe mines caused underground production to surpass that of gem placers. A series of remarkable discoveries of alluvial diamonds reversed the picture and at present placers account for from 55 to 65 pct of the world's production and underground mines for from 45 to 55 pct.

The United States is largely dependent upon imports for its precious stones but the value of such imports varies widely with the prosperity of the country. Comparison of the imports in 1935, a poor year, and the prosperous year 1945 is given in Table 2.

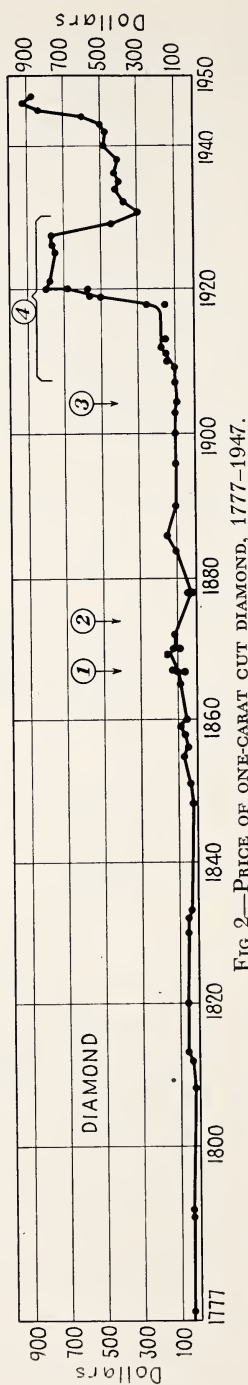
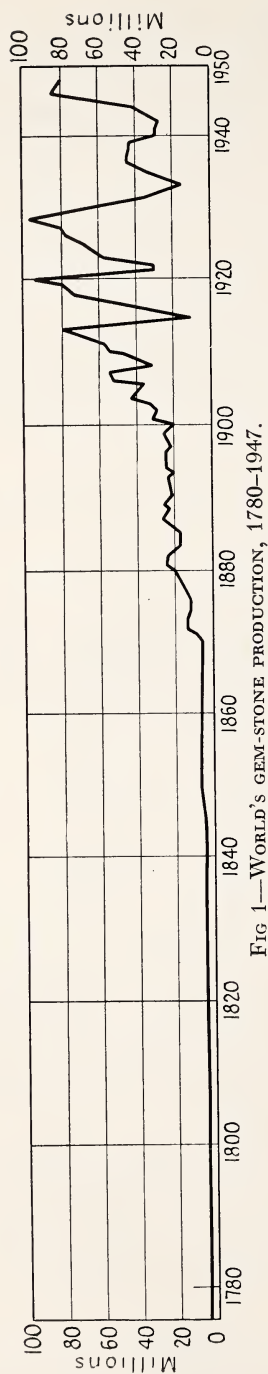
TABLE 2—Imports of Diamonds and Other Precious Stones into the United States

Precious Stones	Duty	1935	1945	1947
Diamonds:				
Glazier's.....	Free	\$4,293,611	\$12,823,962	\$12,840,866
Rough or uncut.....	Free	\$4,261,921	43,122,622	43,051,210
Cut but not set.....	Dutiable	15,538,902	64,185,406	53,471,539
Pearls and parts not strung or set.	Dutiable	652,219	508,495	1,098,716
Other precious stones:				
Uncut.....	Free	50,444	134,698	298,393
Cut but not set.....	Dutiable	1,282,348	5,113,937	3,662,382
Imitation precious stones:				
Except opaque.....	Dutiable	1,480,937	1,052,046	8,290,308
Opaque, including pearls....	Dutiable	30,032	31,136	15,566
Marcasites.....	Dutiable	21,976	104,805	308,724
Total.....		\$27,612,390	\$127,077,107	\$123,037,704

In addition to showing the dependence of imports on our prosperity, Table 2 shows the increased use of industrial diamonds; the growth of diamond cutting in America during the past 11 years and the diminishing demand for pearls during that period.

Being a luxury, precious stones are normally subject to heavy duties, both in the country of their production and that of their consumption. South African diamonds, for instance, pay a 10 pct export tax and gems entering some countries pay a 100 pct import tax. High tariffs foster smuggling, therefore in many countries there is a tendency to reduce import duties on gems.

The Diamond Corporation, through its subsidiaries, the Diamond Trading Co. (gem stones) and Industrial Distributors (industrials), sells from 85 to 95 pct of the world's diamonds and the principal diamond-



1. 1867, South African fields found.

2. 1874, importance of South African fields realized.

3. 1904, Premier becomes a large producer.

4. 1907, Belgian Congo fields found; 1908, Southwest African field found; 1919, Gold Coast fields found; 1930, Sierra Leone fields found.

mining companies are said to be either shareholders in the corporation or to have contracts to sell their product to it. The rough diamonds are sent from the various mines by registered parcel post, the companies carrying a floating insurance policy. The rough stones are sorted in the Corporation's offices, Saint Andrew's Building, London. In good years it disposes of them to brokers and in periods of overproduction and sub-normal demand it builds up its stock. In a good year, sales amount to \$100,000,000 or more.

Almost all gems are sold by the metric carat of 200 mg, although until recently British Guiana used a carat of 205 mg. A brilliant-cut diamond, $\frac{1}{8}$ in. in diameter, weighs about one carat, and one $\frac{1}{2}$ in. in diameter, 9 carats. Because of its lower specific gravity, an emerald of these dimensions would weigh less.

Precious stones have ever been among the most precious of commodities, the noble gems being surpassed in value only by radium and a few other very rare elements. Their value is so concentrated that one could conceal about his person \$10,000,000 worth of fine gems. The value of a gem precious stone is determined by three main natural characteristics—its beauty (either fire, brilliancy, or color), durability, and rarity. A fourth, artificial, is the perfection of its cutting, or, in trade terms, its "make." Less important are: an adequate supply, portability, international market, tariffs, and world economic conditions. These factors determine the value of the noble gems, for which the demand is always relatively steady, and the sales of which are in direct ratio to the world's purchasing power. Fashion, superstition, royal sponsorship, danger of competitive imitations, nationalism, and effective publicity more particularly influence the price of the less valuable gems.

The world has been relatively consistent in its ranking of gems for some 1900 years, for the Romans of Pliny's time valued the diamond first, then the pearl, next the emerald, and finally the opal. Pliny does not give the rating of the ruby and sapphire. The Maharatnani, or the Five Great Gems of the Hindus, for centuries have been the diamond, pearl, ruby, emerald, and sapphire. The Persians in the thirteenth century valued the gems as follows: pearl, ruby, emerald, chrysolite, and diamond. The cutting of that day did not, of course, bring out the full beauty of the diamond.

Fig 2 is a price graph of a one-carat, well-cut, rather fine diamond. From about 26 A.D. to 1872 A.D., a one-carat white diamond was the most expensive stone, except from 1501 to about 1800, when the ruby usurped the lead. From 1872 to the present day, the emerald has been the most expensive stone. The price curves of the emerald, ruby and sapphire are similar to that of the diamond.

Exceptionally fine gems have no fixed price, and, as with fine paintings, set rules do not hold. Such stones are deep-colored "fancies"

(red, green, or blue diamonds), white diamonds of unusual size and water, rubies of over 4 carats, particularly fine emeralds, and unusually fine sapphires. About 1592, Linschoten, the famous Dutch traveler in the Orient, formulated a rule for the valuation of gems; namely, to find the value of a stone of more than one carat, multiply the square of its weight by the value of a one-carat stone of the same quality. This rule still is approximately correct for rubies and emeralds but for the past 70 years, because of the comparative abundance of large diamonds found in South Africa, it has been discarded in diamond valuation. The per carat price of a diamond weighing 3 carats may be twice that of an equally fine diamond of 1 carat; that of a 5-carat stone three times and that of a 20-carat stone, four times. Owing to the relative commonness of large sapphires, Linschoten's rule gives too high a price if applied to that gem. The prices of the other gems are less stable; thus, for example, in the Middle Ages fine amethysts and opals were comparable in price to diamonds.

At present, after the four noble gems, the other precious stones rank in value in descending order about as follows: star ruby, cat's-eye, alexandrite, star sapphire, spinel, black opal, demantoid, kunzite, peridot, morganite, aquamarine, topaz, white opal, jade, tourmaline, zircon, amethyst, garnet, turquoise, citrine, and moonstone. Amethyst, turquoise and garnet are worth from 25¢ to \$2.50 per carat, cut. Most of the precious stones not listed are worth still less and in some jewelry the value is in the workmanship rather than in the material. It should, however, be added, in fairness to precious stones, that 25¢ a carat is equivalent to \$567 per avoirdupois pound (\$1250 per kilo). Americans of today use and love many gem stones that were unknown to their fathers.

EXPLORATION, MINING AND MILLING

In normal years, gem mining employs some 150,000 men, of whom one fifth are whites and the rest African blacks or other races of color. In describing gem mining and milling, one must differentiate between the operations of the native miner and that of the companies. The former is primitive and has changed little in centuries; the latter are well conducted up-to-date mining operations, which make progress yearly. The native, as a rule, dispenses with prospecting, although he may locate ruby-bearing or sapphire-bearing gravel by forcing a soft iron bar into the ground and noting whether the iron is scratched. Usually he finds his deposit by the trial and error method and if a shaft that he believes to be well located proves unprofitable, he is sure that the gods or the spirits of the mine are unwilling to disgorge its wealth.

Kimberlite pipes in South Africa are relatively common but only a small percentage of them contain a profitable diamond content. Geo-

physical methods of prospecting can outline such pipes but such surveys are of relatively little value, as they can indicate nothing as to grade. The presence of alluvial diamond deposits near a pipe may be encouraging but large-scale washing tests alone can prove whether development of a pipe is warranted. The large companies mining alluvial diamonds block out their gravel by systematic prospecting. This may consist of test-pitting on 10-m or 100-ft squares, careful note being taken of the thickness of the overburden and of the pay gravel and of the nature of the bedrock. The gravel samples washed are large. In certain stream valleys, trenches across the entire valley at distances of, say 100 ft are more convenient. Drilling may be used in water-logged ground, although the sample recovered is too small to be of much value except in such fields as that of the Kasai Basin (Belgian Congo), where the diamond content is proportional to the percentage of certain of the heavier and more common "satellites" accompanying the diamond.

The native producer usually obtains his gravel by surface digging, or, if the overburden is thick, by sinking a pit to the gravel horizon and then extracting as much of the surrounding gravel as he thinks safe. The process is repeated as necessity requires. Either no timbering is done or it consists of simple shoring with small timbers. Hoisting usually is done in baskets and drainage by a kerosene tin on a sweep. In the Afghanistan lapis lazuli, the Burmese jade mines, and certain of the Indian diamond mines, fire setting is employed. Boulders or gravel in the larger stream beds are, in instances, recovered by divers, who descend on a rock-weighted rope.

The South African pipe mines were started as opencuts but all of them are now underground mines, the depth of economic and safe opencut mining having been exceeded. The Premier mine, now being re-equipped as an underground mine, is a huge opencut about $\frac{1}{2}$ mile long, $\frac{1}{8}$ mile wide and 660 ft deep, marked out in benches 50 ft high. When operated at capacity, Premier was one of the world's large-tonnage mining operations. In the underground mines, a shaft is sunk in the country rock at a safe distance from the pipe and main haulageways are driven to the pipe at stated vertical intervals. From the haulageway, drifts are driven through the pipe 40 ft apart and smaller drifts cross these at right angles. The blue ground is caved up to the next level, retreating from the far side of the pipe. At a certain distance from the far wall, a series of steplike levels is formed. The blue ground is trammed to the shaft, dumped into ore pockets and hoisted.

The important alluvial diamond-mining companies, according to local conditions, remove overburden by sluicing, by hand, or by mechanical shovels.

The simplest milling is that of the Indian diamond miner, who crushes his ore with a sledgehammer, washes out the mud and fines,

spreads the remainder on a flat surface and picks and repicks it for diamonds. Tavernier, however, at the Kollūr mine, found that the finer materials were winnowed dry several times in a basket and then hand-sorted. The Singhalese gem hunter concentrates his gravel in a near-by stream in a rattan basket and then hand-sorts the concentrate. The Borneon diamond miners sit at either end of a trough filled with water and clayey gravel, forcing the mass backward and forward with their feet. The larger pebbles are thrown away. The gravel is then sized with a sieve and concentrated in native pans and the concentrate is hand-sorted. The British Guiana "pork-knocker," as the local colored prospector is called, adds water to his gravel and hoes it through an iron plate containing $\frac{3}{8}$ -in. holes. The oversize is thrown away and the rest is concentrated on a sieve with $\frac{1}{16}$ -in holes. The Brazilian native worker places his gravel in a three-sided compartment sloping toward the stream. He throws water on the gravel, to remove the lighter particles, concentrates the remainder in a batea, and hand-picks the concentrates.

In South Africa, the blue ground from the pipes was formerly "farmed" for from 6 to 18 months, by the end of which period most of the rock had weathered to a clay. Now, however, it is crushed in stages, with corrugated rolls. The crushed rock passes to pans 14 ft in diameter equipped with rotating arms fitted with knifelike blades. The heavier particles, including the diamonds, fall to the bottom of the pan, where they are forced to the perimeter and drawn off periodically. The lighter material flows over a weir at the central core. The pan concentrates, about 2 pct of the "blue ground," are sized and then jigged. These jig products formerly were hand-picked, mainly by native criminals, but now are fed to a grease table, which consists of a steplike series of bronze, corrugated plates sloping gently, covered with a coating of grease. The table has a lateral, oscillating motion. Water and the concentrates are fed at the head of the table and a treatment and re-treatment results in an almost perfect separation of the diamonds, with a little pyrite, ilmenite, ruby and sapphire. The grease, together with the embedded stones, is then scraped off the table and placed in a wire basket, which is immersed in boiling water. The diamonds are treated with acid and alkalis and the screened to size and sorted by hand. A shipment is divided into about 10 classes as to shape and purity and the more valuable divisions are further classified into 8 colors. Each subdivision is placed in papers, packed in boxes, carefully sealed, and sent to London by registered mail. At the Diamond Corporation's offices, the packages are re-sorted, a large shipment sometimes being divided into more than one thousand subdivisions.

Some of the larger diamond units are experimenting with sink-and-float separation.

In the large alluvial diamond mills, those of the Belgian Congo,

for example, the gravel, if very clayey, is first puddled, then sized by trommels. The undersize is rejected and the oversize is sent to the dump. Occasionally it passes over picking belts en route. The intermediate product is concentrated in pans from 5 to 14 ft in diameter and the concentrate is jigged, the Harz type of jig being common. In certain instances, magnetic separators remove magnetite and other magnetic "satellites." The concentrate is then delivered to containers, which are locked and trucked to a central picking station. This concentrate in the Congo mills is about 0.10 pct of the feed.

Superintendents of operating gem properties must be much more vigilant than those of gold mines, to guard against "high grading." In the more modern mills, the later milling units are locked and access to them is permitted to only the most trusted employees. While the chance of a diamond being seen as blue ground or gravel is being mined is normally small, all black employees of the South African pipe mines spend the term of their enlistment (three or six months) in compounds. Here they are well housed but are effectively separated from the outside world by wire fences. When their term is about to be finished, they are purged or X-rayed to be sure they have not swallowed diamonds or concealed them about their person. The natives employed in the sorting plant at the Burma Ruby Mines Ltd. were compelled to wear boxes over their heads, with gauze windows, so that they could not swallow the gems. At best, however, thefts occur, in direct ratio to the primitiveness of the mining methods.

Mining and milling costs in gem mining are so variable, owing to the individual characteristics of each deposit and to varying scales of operation, that such figures are of little value. In 1945, costs at De Beers mines varied from 4s 9.06d to 5s 0.44d per load (16 cu ft of blue ground in place).

CUTTING

Most gem stones before they are used in jewelry are cut or artificially shaped. The art of the lapidary is ancient. It was practiced in Egypt and in the Mesopotamian Valley at least 5500 years ago. The ancient lapidary shaped the stones into scarabs, lenticular or other forms, and then engraved on them characters, figures or scenes. Such intaglios were used as seals. About 500 B.C., fine banded agates began to be cut with figures in relief, each of the variously colored layers being used for part of the design. These cameos were used for decorative purposes only. The only gems the Roman lapidary faceted were the beryl and the emerald, but even to this day the Chinese lapidary, the leader of all sculptors of hard stones in the round, does not facet stones. The cabochon cut, so suited to the star sapphires and rubies, garnet, turquoise, opal, and moonstone, is one species of sculpture in the round still practiced by the Western lapidary. Work in the round, however, fails to

bring out the beauty of transparent gems possessing "fire," and gem cutting requiring the faceting of such gems is most effectively done in Europe and in America. The art of faceting was commonly employed in Europe more than 500 years ago and is still being improved. It originated, however, in India, perhaps 2000 years ago, with the crude shaping of cleavage fragments (*lasques*) and the polishing of natural crystal faces (*naifes*).

In the process of diamond cutting, after careful study the piece of rough is first given an octahedral shape by either cleaving or sawing. Bruting follows, giving the stone the shape of the brilliant with incipient facets. This is done by rubbing two stones against one another. Polishing, by which the facets are perfected and smoothed, follows, and it is done on a soft iron wheel, fed with olive oil charged with diamond dust, the wheel making about 2500 revolutions per minute. Antwerp and neighboring parts of Belgium have some 22,000 diamond cutters; Palestine, 4500; and New York, 4000.

Normally, there are some 30,000 diamond cutters, most of whom live in Low Countries. In the spring of 1940, this industry was destroyed but in the aggregate an equally great industry mushroomed in neutral countries. In 1946, with the rebirth of the Belgian industry, cutting was hugely overstaffed, as there is no more gem production than in the mid-twenties, the increase in production being in industrial grades. In addition to the industry of the Low Countries, those of America and of Palestine and perhaps one or two more may survive.

Such colored stones as are not cut cabochon are usually fashioned into trap or step-cut gems. In plan, this cut is oblong with a table above, parallel to which are several sloping facets down to the girdle; while below the girdle are a number of similar facets, becoming smaller as the outlet is approached. The noble gems except the diamond are usually cut in London, Bombay, Colombo, New York, or Paris. The cheaper stones, particularly the agate, are cut in Idar and Oberstein, Germany; in the Jura Mountains, France; in the United States, and in Russia. Czechoslovakia specializes in cutting garnet and imitation stones and China in jade.

THE DIAMOND

The diamond, the most desired of precious stones, is commercially by far the most important gem and the only one, with a rare exception, to which modern mining and milling methods are applied. Chemically it is pure carbon, therefore it will burn if heated in oxygen, but aside from this it is an extremely stable body. It crystallizes in the cubic system. The diamond varies from colorless and transparent through slightly tinted yellows, grays, and browns to virtually opaque black stones. Deeply colored stones of attractive colors, especially blue, green, or red, are known as "fancies" and are the most valuable of all gems. The diamond is the

hardest substance in the world. It cleaves perfectly parallel to the octahedron and the myth that it will resist the blow of a hammer has on occasions proved to be the most expensive of misstatements. Its rather high specific gravity (fine gems, about 3.52) accounts for its concentration by nature in gravels and by man in his pans and jigs.

The diamond owes its brilliance and "fire" when skillfully cut to its high refractive index and to its dispersion, greater than that of any other colorless gem.

Hindu legends would lead us to believe that the discovery of diamonds in India, the oldest known diamond field, predates the birth of Christ several millennia, but a study of early Oriental commerce suggests that the first Indian stone attracted the eye of some native crossing a pebble-bottomed stream not earlier than 800 B.C. The oldest bediamonded artifact known to us is a little bronze Greek goddess (British Museum, Bronze No. 192) with eyes of diamond crystals dating from about 480 B.C. In this and other collections, a number of Roman rings set with rough diamonds are preserved but most of these postdate the beginning of our era. About 79 A.D., Pliny gave what we may call a scientific description of a gem so valuable as to be "known only to kings."

While the Romans valued it as the most precious of all things, the diamond did not really begin to come into its own until the Middle Ages, for not till then had the art of diamond cutting progressed sufficiently to bring out more than a modicum of the stone's fire. Its popularity also grew with the ever increasing improvement in the lighting of homes at night. The increase in wealth has permitted the average citizen of our time to possess a stone that 500 years ago was the insignia of great wealth. Its popularity has further been high-lighted by countless colorful gem lovers, notably by Charles the Bold, Agnes Sorel, Cardinal Mazarin, the Empress Eugenie, and, indeed, by every civilized woman. Agnes Sorel was probably the first woman to wear the gem, it having been almost exclusively the ornament of kings and men of wealth before her day.

The diamond became relatively common only in the fifteenth century and even in the first half of the nineteenth century the value of the world's production did not exceed \$1,500,000 to \$4,000,000. South Africa's marvellous mines raised the figure in the eighties and nineties of the last century to \$20,000,000. Before the depression between the two World Wars, 7,000,000 carats worth \$70,000,000 to \$85,000,000 at the mine was perhaps an average year's output. If it were possible to fuse a year's production into a cube, it would be about $2\frac{1}{2}$ ft on a side, won from gravel or rock 774 ft on a side; in other words, some 34,000,000 units of rock or gravel are treated to recover one unit of diamond—a minuscule reward for some 125,000 laborers.

TABLE 3—*Diamond Production for Typical Years*

Producers	1912		1925		1933		1947	
	Carats	Pct by Wt	Carats	Pct by Wt	Carats	Pct by Wt	Carats	Pct by Wt
South Africa: mines	4,888,575	76.2	2,190,871	50.3			918,042.50	9.4
Alluvial	183,307	8.4	239,257	6.2	506,552	12.6	286,691.76 ^a	3.0
Total	5,071,882	84.0	2,430,128	56.5	506,552	12.6	1,204,734.26	12.4
Southwest Africa	992,380	11.8	515,000	11.3			180,739.00	1.9
Tanganyika Territory							92,229.00	1.0
Belgian Congo			885,000	20.01	1,931,172	48.2	5,474,468.62	56.1
Angola			100,000	2.3	373,629	9.3	799,209.71	8.2
Gold Coast			100,000	2.3	1,100,000	27.4	852,493.00 ^b	8.8
Sierra Leone					32,017	0.8	605,554.00	6.2
French Equatorial Africa							90,000.00 ^c	0.8
French West Africa							90,000.00 ^c	0.8
British Guiana	7,300	0.2	220,000	5.0	30,000	0.8	24,669.44	0.3
Brazil	100,000	1.6	100,000	2.3	34,000	0.9	275,000.00 ^c	2.8
Miscellaneous producers	6,600	0.1	10,000	0.23	4,025	0.1	65,134.00 ^d	0.7
Total	6,178,162	100.00	4,360,128	100.00	4,011,395	100.00	9,754,231.03	100.0
Value at mine	\$57,943,400		\$58,549,083		\$14,754,012		\$75,105,000.00	
Value per carat	\$9.38		\$13.40		\$3.68		\$7.70	

^a Includes an estimate of 100,000 carats for State Mines of Vamaqualand.^b Exports.^c Estimated.^d Includes 61,634.45 carats from Venezuela and also small productions of India, Borneo, New South Wales, and sporadic finds in Russia and USA.

Production of Diamonds

The demand for gem diamonds continues to increase from decade to decade and its growth was emphasized by World War II. Large sales of industrials began only about 10 years ago. Since the war, stocks of all grades of diamonds have been depleted.

The world's all-time diamond production to Dec. 31, 1946, has been some 380,000,000 carats (83.8 short tons), of which about 160,000,000 carats (35.3 short tons) have been cuttables and 220,000,000 carats (48.5 short tons) industrials. Owing to cutting and other losses, there remain in the world, cut of all qualities, perhaps 64,800,000 carats worth some 10 billion dollars. By weight, the producers in descending order have been South Africa, Brazil, India and the Belgian Congo; by value, South Africa is far in the lead.

The year of largest production was 1945, the yield being some 14,250,000 carats, of which 82 pct was bort. Indeed, for some 25 years the production of gem grades has averaged about 2,500,000 to 2,750,000 carats (Table 3). The marked variation in the price per carat from year to year is due to two factors, the quality of the diamonds produced and the condition of the diamond market. During the past decade, 75 pct of the rough sold has been industrials, they from year to year making up by weight 60 to 83 pct of total sales. In 1946, the Belgian Congo by weight produced 59 pct of the world's diamonds and by value 11 pct; the British Empire, by weight 28 pct and by value 70 pct. In that year, 1188 lb of gem grades and 3316 lb of industrials were produced. More than 95 pct of the production is from the African continent.

Until 1870, all diamonds came from placer mines, but from 1878 to 1921 the South African pipes dominated the production. Since 1907, five remarkable alluvial fields have been found and since 1922 placer production has again exceeded that of the pipes. Table 3 shows how diamond production has shifted in the past 35 years; in part, the figures are estimates.

In size, diamonds vary from microscopic crystals to the fist-big Cullinan diamond, which weighed $1\frac{1}{3}$ lb (3106 carats). The average stone recovered is less than $\frac{1}{16}$ in. in diameter. Size varies from deposit to deposit in alluvial diamond fields and from pipe to pipe and in cases in different parts of the complex intrusion making up a single pipe. India, South Africa, Borneo, Sierra Leone and the Bagagem district, Brazil, are the fields producing large stones.

Similarly, the various diamond fields produce stones of different quality, although there is little if any difference in the better stones from any field. The percentage of fine stones, however, may in one mine be large and in another small. Accordingly, at present the run-of-mine stones from one field may be worth but \$2 a carat and from another \$40.

On the average, the quality of Indian stones is perhaps better than that of Brazilian diamonds and that of the latter, at least as good as that of the stones from Africa.

Each South African pipe produces characteristic diamonds and one familiar with the stones can with certainty, if shown a typical parcel, name their source. The variations are in purity, size, shape and color.

Only a small part of a normal year's production (Fig 3) is suitable

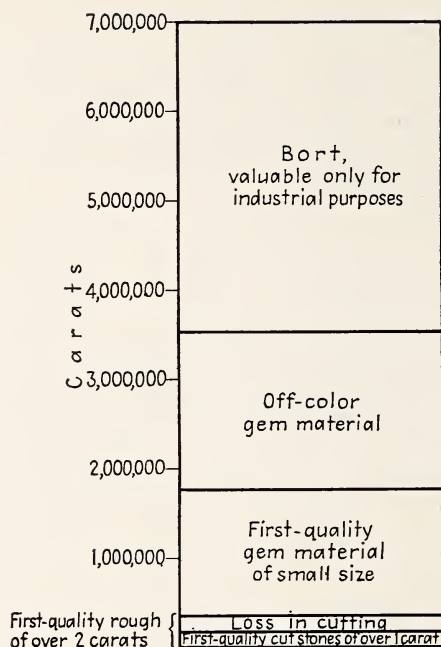


FIG 3—MAKE-UP OF WORLD'S DIAMOND PRODUCTION IN A NORMAL YEAR.

for cutting into fine gems. More than one half is bort, material so off-colored or so badly flawed that it can be used only industrially. A third quarter is off-color or flawed but can be cut into rather showy jewels, eagerly purchased by the Indian, South American and eastern European trade. The fourth quarter is colorless gem material but much of it is small and can be cut only into jewelry mountings. Only about 5 pct of the total is fine, large rough weighing 2 carats or more, producing after cutting (cutting loss normally about 55 pct) fine gems of one carat or more. As some of the cut stones exceed 10 carats in weight, and many weigh over 2 to 4 carats, there are available for sale each year only about 100,000 fine large diamonds. In consequence, even in years of poor sales, fine large diamonds were at times difficult to procure.

The known reserves of diamonds are not very large, being of the order of those of zinc or lead rather than that of copper, nickel or coal.

The pipe mines normally have blue ground partly developed, above

a datum level, equivalent to from 3 to 5 years output. The more important mines undoubtedly have a long life ahead of them, although with depth it seems to be a rule that the pipes decrease in size, as does on the average diamond content. Many of the South African alluvial fields have already been exhausted and alluvial mining in South Africa presumably has passed its peak. The Southwest African, the Congo-Angola and the Gold Coast fields have gravel blocked out for a dozen year's operations and probably will not be exhausted for a further 10 to 20 years. Each year as prospecting continues the chance of the discovery of new fields becomes less likely, although such discoveries, rather than the artificial production of the stone, is a menace the industry faces.

In Africa, about half the production by value is obtained directly or indirectly from Cretaceous kimberlite pipes and the other half from the weathering of pre-Cambrian rocks, the direct source being unknown.

The diamond, while it occurs in only a few places in commercial quantities, has been found in all five of the continents.

Occurrence of Diamonds

The common occurrence of the diamond is as a pebble in gravel, a secondary source varying from gravel to thoroughly cemented conglomerates and ranging in age from present river or marine benches to hard pre-Cambrian rocks. The classic example of a source rock from which such pebbles are derived is that of the pipe mines of South Africa, where the diamond occurs as a crystal, in a dark, greenish, basic igneous rock called kimberlite. This occurs as a vertical, steep-sided, funnel-shaped mass of rock, which has been forced from below through a series of flat-lying sedimentary rocks. The cross section of the pipe is as a rule circular or elliptical and its diameter varies from a few tens of feet to about 2300 ft, with the surface exposure from less than an acre to over 80 acres. Kimberlite pipes and dikes occur over a vast area in South Africa, Southwest Africa, Rhodesia, Tanganyika Territory, and southeastern Belgian Congo, there being hundreds of them. Some are barren of diamonds, some contain a few but not enough to pay, while the number having a commercial diamond content is very small. At the outcrop of the pipes that have been worked there was a notable enrichment of diamonds, due to the blowing away of the lighter components of the decomposed rock by the wind. In the unaltered rock in virtually all the pipes, the diamond content decreases with depth; that is, the present surface appears to have been the horizon of maximum diamond deposition. Elsewhere diamonds occur in still more basic rocks, including both stony and iron meteorites. In South Africa and in Australia, diamond has been found in andesites. Certain of the upland deposits of Minas Gerais, Brazil, appear to be igneous breccias, the highly altered matrix

of which presumably is andesitic, if not more acid, in composition. The presence of diamonds in granitic rocks and in some regional or contact-metamorphic rocks is unproved, but is far from impossible. In short, the diamond is a mineral of multiple sources although kimberlite is so dominant commercially that its importance is usually exaggerated.

Diamond Fields

India—India is the oldest known diamond field and was the dominant producer until 1725. In the seventeenth century, the production may have reached in certain years several hundred thousand carats. All the stones are pebbles in either pre-Cambrian conglomerates or modern gravels.

Borneo—The Borneo fields were discovered between 600 and 1000 A.D. and late in the seventeenth century probably produced 50,000 carats a year. The stones occur in river gravels. They are fine, a black gem stone being prized throughout the East for mourning jewelry.

Brazil—Diamonds were recognized in 1720 in the gold placers of Diamantina, Minas Gerais. Later deposits were found in Bahia, Matto Grosso, Goyaz and other states. Total production has approximated 17,500,000 carats worth some \$150,000,000. The field's history has been an interesting example of governmental interference with private enterprise. Mining is now carried on by prospectors or syndicates and to date no foreign company has been particularly successful. The diamonds, which are of excellent quality, occur in present-day streams and in ancient elevated terrace gravels, in ancient conglomerates and apparently in igneous breccias. Basic rocks allied to kimberlite are reported in certain districts. Bahia is the sole producer of carbonado.

South Africa—The discovery of diamonds in South Africa in 1867 changed a country on the verge of financial ruin to a prosperous country and it was the profits from the diamond deposits that financed the Rand gold field and permitted Cecil Rhodes to push the British flag northward almost to the equator.

South Africa to Dec. 31, 1946, produced (in addition to stolen stones) diamonds to the value of some £355,500,000, say one fourth of its gold production. Peak production was in 1928 (£16,677,772), since when production has fluctuated markedly. Of De Beers' pipes, Dutoitspan and Bultfontein are operating, Wesselton is ready to produce and Premier and New Jagersfontein are being re-equipped. In normal times these mines employ about 18,000 blacks.

About 20 years ago South Africa's alluvial production seemed to be stabilized at from 150,000 to 250,000 carats a year but in 1926 the excessively rich Lichtenburg (Transvaal) alluvials were discovered. For four years the production was huge. In the Transvaal and the Cape Colony alluvial fields, mining is carried on by diggers and ill-financed syndicates and on average is unprofitable.

In 1925, diamonds were rediscovered in certain marine terraces in Namaqualand south of the mouth of the Orange River. It was soon realized that these deposits were not only rich but produced magnificent stones both as to quality and size. De Beers owns part of the field but the Union operates the more important portion.

Southwest Africa—When diamonds were found in 1908 in what was then German Southwest Africa, the Germans fought the British unsuccessfully for control of the diamond market. The present owners, the Consolidated Diamond Mines of Southwest Africa, produce a splendid assortment of industrials and gem stones. The pay gravel on the whole is relatively low grade but locally wind action has caused rich surface concentration. The pay varies in thickness from a few inches to as much as 30 ft. Before the World War, this field reached a peak production of 1,500,000 carats.

Central Africa (Belgian Congo-Angola)—In 1907, a Forminière prospector panned a diamond from the middle reaches of the Kasai River. In 1913, more important finds followed and eventually diamonds were traced up the same drainage into Angola. In the Belgian Congo, there are four operating companies and in Angola one—Diamang. In part the stones are of excellent quality and average from 6 to 12 per carat. From the surface downward is overburden, pay gravel and bedrock. Pay may be from 3 to 7 ft thick and 1 to 4 cu m of overburden is handled per cubic meter of gravel. The gravel carries from $\frac{2}{3}$ to $\frac{3}{4}$ carats per cubic meter. The original source of the diamonds is unknown. The stones, however, are derived from Jura-Trias conglomerates and hence, like the Gwelo Forest (Rhodesia), the Rand Gold mine diamonds and the Gold Coast diamonds long antedate those of the kimberlite pipes.

The B.C.K. alluvial deposits to the east of the Kasai drainage are the richest diamond deposits in the world as to content, although 95 pct of the product is crushing bort. The satellites differ widely from those of the Kasai alluvials and recently diamond-bearing kimberlite pipes have been found near the alluvials, presumably the source of the diamonds. This deposit accounts for the fact that the Belgian Congo has produced by weight since 1930 two thirds to three fourths of the world's diamonds.

Gold Coast—Diamonds were found in 1919 in the Gold Coast by Sir A. E. Kitson. The Coast is a large producer of small good-quality stones, many of which are fine drilling borts.

Sierra Leone—In 1930, the colonial geological survey found diamonds in Sierra Leone. By 1937, the production reached 913,000 carats. The product is in part fine and large gem material and in part industrial stones. The deposits lie on granite, often near basic sheets or dikes.

Tanganyika Territory—The occurrence of diamonds in Tanganyika Territory was known some 40 years ago. The relatively small production increased markedly during the second World War and the colony now has a fairly important production of fine gem stones.

Minor Sources—British Guiana, Venezuela, Rhodesia, French Equatorial Africa, French Guinea, Shan-tung and Australia have produced a few diamonds. Diamonds have been found in a number of localities in the United States. They occur as mineralogic curiosities in Virginia, North Carolina, Georgia, and other southeastern states; a number have been recovered from gold sluices in California and isolated finds are reported from Oregon and several of the Rocky Mountain states. Near Murfreesboro, Arkansas, is a stock of kimberlite, which has produced several thousand diamonds, but the deposit does not appear to be commercial. In the terminal moraine of the last glacial epoch in Wisconsin, Illinois, Indiana, Michigan, and Ohio, diamonds have been picked up here and there by the merest chance. The stones are of excellent water and of fair average size. There is, therefore, to the north in Canada an original source of fine diamonds, although of course we are ignorant as to whether it carries enough stones to pay.

RUBY AND SAPPHIRE

The ruby and sapphire are, respectively, the red and blue transparent varieties of corundum—crystallized alumina. "Sapphire" also includes all other colors except red, that color being placed before sapphire. Formerly misleading names, "oriental topaz," "oriental emerald" and "oriental amethyst," were applied to these gems. As the dispersion of the corundum gems is low, they lack "fire," but they are valued for their fine colors. "Pigeon's-blood" red and a deep cornflower blue are preferred. Ruby of fine quality rarely occurs of any appreciable size but fine sapphires of considerable size are relatively common. Some rubies and sapphires are characterized by parallel fibrous structures and when this structure is highly developed and the stone is cut cabochon, a white six-pointed star floats in the stone. Such stones are called star sapphires or rubies. The color is normally bluish gray or grayish pink and fine reds or blues free of a milky caste are rare. Since the war began, the price of star stones has sky-rocketed.

The finest rubies come from Burma. The mines, which were worked at least as early as the fourteenth century, center about Mogok. Ruby and spinel occur in a contact-metamorphosed limestone associated with gneisses and schists, the complex being intruded by both acid and basic granular igneous rocks. The limestone is too poor to work but talus gravel derived from it and the flooring of caves in it may be commercial. The principal source is "byon," a pebbly clay usually covered with some 15 ft of overburden. The layer next to bedrock is frequently rich. An English company, Burma Ruby Mines Ltd., worked the field from 1889 to 1931, but while its total production was relatively large, the enterprise was on the whole unprofitable. The present production by natives

is relatively small. Besides rubies and sapphires, spinels, blue tourmalines and a number of other gem stones are recovered as by-products at Mogok.

Ceylon for at least 2500 years has produced sapphires and some rubies and from it, and to a lesser extent from Burma, come star sapphires and rubies. The rubies generally are pale in color but the sapphires frequently are fine, although paler than those of some other gem fields. The gems occur in the gravels of broad stream beds, the original source of the rubies and of some of the sapphires being crystalline limestone and others being derived from gneisses and schists. The gravel in instances extends to a depth of 120 ft. Gems are especially abundant in the lower gravels, particularly in depressions in the bedrock. Spinel, chrysoberyl, topaz, zircon, garnet, tourmaline and a number of other gem stones are by-products of sapphire mining.

Southern Siam and contiguous parts of Cambodia have gem fields that produce sapphires and some rubies, the latter having a purplish brown tint. Although, because they are exported via Siamese ports, the stones are sold in Europe as Siamese stones, the majority come from Cambodia. This region, once an important producer, is reported to be approaching exhaustion. Rubies occur in crystalline limestone in Afghanistan and Badakshan.

Fine, deep blue sapphires occur in a pegmatite dike in the Zanskar Range, Kashmir. First discovered in 1908, it was energetically worked from 1924 on, the production being in certain years several million carats. Sapphire occurs in the gravels of New South Wales at several places, notably in the Inverell district. The Anakie field in Queensland is more important, however. The sapphires are inky blue and appear in artificial light almost black. Yellow or sage green sapphires also occur, and an occasional ruby. The stones occur in old gravel deposits elevated above the present stream beds. The field was discovered in 1870 and reached its peak production (\$320,600) in 1920.

Rather pale sapphires with a steely luster, and also rubies, are recovered from stream gravels in Granite and Powell Counties, and near Helena, in Montana. They were also mined from a monchiquite-camp-tonite dike in Yogo Gulch, Fergus County, Montana. Operations ceased in 1929. Several hundred thousand carats were produced annually some 10 years ago but only one fourth was of gem grade, the rest being used industrially, largely for watch jewels. Synthetics have since supplanted them.

The demand for gem stones exceeds the current supply: in consequence we look to old jewelry to offset the shortage.

Synthetic rubies and sapphires are used in cheaper jewelry. Recently, beautiful star stones have been made synthetically.

EMERALD, AQUAMARINE, YELLOW BERYL, AND MORGANITE

Emerald, aquamarine, yellow beryl, and morganite are all members of the beryl family, a silicate of beryllium and aluminum, which characteristically crystallizes as six-sided prisms. They are fairly hard (7.5 to 8), but the other physical characteristics are not striking, and the gem varieties owe their beauty to their color and transparency.

The deep grass green, velvety variety of emerald is the most valuable of all precious stones, but probably no unflawed emeralds of fair size exist. Practically all fine emeralds come from the Muzo or Cosquez mines in Colombia, both owned by the Government, which from time to time has farmed them out. Emerald with calcite and a number of other gangue minerals occurs in veins of pneumatolytic origin, which cut in all directions highly folded black carbonaceous shales, presumably of Lower Cretaceous age. The Chivor deposit is somewhat similar, although albite and quartz are the principal gangues and the color of the gems is not so fine. At many of the other emerald occurrences, the gem occurs in schists near pegmatitic intrusions, the causative rock—for instance, the Ural Mountains, the Egyptian, the Habachthal (Austria), the South African and the North Carolinian occurrences. Some of the Australian deposits are of this type but the gem also occurs in pegmatite dikes. The emeralds at Bahia, Brazil, occur with quartz and calcite in cavities in crystalline limestone. Next to those at Muzo, the Russian stones are best, but on average do not compare with the Colombian in fine deep color.

The other gem varieties of beryl—aquamarine, the sea-green variety, golden beryl, the yellow, and morganite, the rose pink—occur as constituents of pegmatites or in gravels derived therefrom. Brazil, Madagascar, Southwest Africa, the Urals and the Transbaikal district (Russia) are the principal sources.

Newly mined emeralds do not fulfill the demand and many emeralds are recovered from old jewelry. Prices in the past decade have increased greatly.

Chrysoberyl and Its Varieties, Cat's-eye and Alexandrite

Chrysoberyl is a pleasing greenish yellow gem. Cat's-eye is a variety containing many parallel fibers, which, when the stone is cut cabochon, exhibits marked chatoyance. The groundmass of the gem is honey (greenish) yellow and the "pupil" whitish. Alexandrite is a most intriguing gem, being bluish green or dark green by natural light and raspberry red by artificial light. The Ceylon gravels are the most productive field of all three varieties but alexandrite was first found in the Urals and Brazil also produces chrysoberyl. The stones are of pegmatitic origin although the immediate host rock may be gneiss or schist.

OTHER GEM STONES

Spinel—Spinel has two gem forms, the rose-bed balas ruby and the spinel ruby, of ruby color. Indeed, the Black Prince's ruby, in the English Regalia, which has not without reason been considered by some as the most beautiful gem in the world, is in reality a spinel ruby. Ceylon, Burma, Afghanistan and Siam are the principal localities. Spinel usually occurs in contact-metamorphic limestone or in gravels derived from them.

Spodumene—Spodumene has three attractive gem forms: (1) the rare yellowish green hiddenite from North Carolina, (2) the more common yellow from Brazil, and (3) the rose or lilac-pink kunzite from near San Diego, California, and from Madagascar. Because of the perfect cleavage, the gem is difficult to cut. It is of pegmatitic origin although some of the gems are recovered from gravels.

Opal—The opal is a transparent to translucent gem traversed by myriads of tiny fissures or tiny veinlets of later opal, which reflect and refract the light, resulting in a lovely play of all the colors of the rainbow. The ground may be colorless to almost black, the latter type being particularly esteemed. Hungary (now Czechoslovakia) was once the principal source of opals but the Australian gems are much finer than the Hungarian. The all-time output of Australia (largely New South Wales and South Australia) exceeded £2,000,000.

Topaz—Topaz shows some "fire" and the colorless blue, sherry yellow and pink varieties are rather attractive gems. The rose-pink variety is usually a yellow stone changed in color by careful heating. Brazil and Siberia are the principal sources. The gem occurs usually in pegmatites or in gravels derived from them.

Peridot—Peridot is the transparent olive-green variety of olivine and chrysolite, the greenish yellow variety. While an attractive gem, it is too soft to be used where subject to much wear. The finest come from Zebirget Island, in the Red Sea.

Tourmaline—Tourmaline appears in practically all colors and frequently is particolored at right angles to the main axis of the prism or zonally parallel to that axis. The deep green and rose pinks are particularly attractive, Maine, California (near San Diego), Brazil, Madagascar, Burma and Russia are the principal producers. The gem is typically a pegmatitic mineral, although it is also recovered from gravels.

Zircon—Zircon, because of its high refraction and great dispersive power, has next to the diamond the greatest "fire." It occurs colorless ("matura diamonds") and yellowish red (jacinth). Certain brown Siamese stones when heated change to a sea-green blue—permanently or temporarily. Siamese, Ceylonese and Australian gem gravels are the principal sources of supply.

Garnet—The garnet family includes several members that are

used as gems, notably pyrope (blood red with a yellowish tinge); almandine (violet-tinged crimson); hessonite (orange yellow); demantoid (emerald green, with highly developed "fire"); and spessartine (orange red). They occur in a variety of igneous and metamorphic rocks and in gravels and in many different countries. The attractive raspberry-red rhodolite from North Carolina should be mentioned.

Turquoise—Turquoise, although opaque, is attractive because of its robin's-egg-blue color. Probably the first large-scale mining was that of turquoise in the Sinai Peninsula. The stone had also been a great favorite of the American Indians for centuries before the white man arrived on the continent. Persia and our own Southwest are the principal sources of supply.

Jade—Under the name "jade," two distinct but quite similar minerals, nephrite and jadeite, are included. An emerald green is the most desired color, although it occurs also in other shades of green as well as yellowish and black. The stone varies from translucent to opaque. Always a favorite in China and India, it became popular in the West a generation ago. The principal localities of nephrite are Chinese Turk-estan, Russia, New Zealand, and the United States, and that of jadeite, Burma. Nephrite occurs in regions of metamorphic rocks and jadeite as an albite-jadeite intrusive rock. Both occur as stream gravels.

Lapis Lazuli—Like turquoise, lapis lazuli is opaque and its beauty depends upon its color, a deep Prussian blue. Afghanistan is the principal locality.

Amber—Amber is the fossil resin of a pine tree and was one of the earliest decorative substances used by man. Its pleasing yellow transparency is well known to all. It is extensively mined on the Prussian coast and occurs in many other parts of the world.

Quartz and Feldspar—Space permits only mention of the more beautiful members of the quartz family: the limpid rock crystal, the purple amethyst, the yellow citrine, the apple-green translucent chrysoprase, the red carnelian, and the banded agate. Among the feldspars the moonstone, with its intriguing opalescence; labradorite, with its varying iridescent blues, grays and greens; and the green amazonstone, are the finer varieties.

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CHAPTER 36

PUMICE AND PUMICITE

BY JAMES A. BARR, JR.*

PUMICE and pumice are varieties of volcanic ejecta formed from lavas of the more silicic types. Chemical analyses of pumice, pumicite and perlite, from which synthetic pumice is now produced, will generally fall within the limits 65 to 75 pct silica, 9 to 20 pct alumina, less than 8 pct combined alkalies (sodium and potassium oxides), less than 3 pct calcium and magnesium oxide, less than 3 pct iron oxide, with smaller amounts of manganese, titanium, phosphorus and other oxides. Perlite is characterized chemically by having, in addition to the percentages of oxides given above, as high as 6 pct combined water.

PROPERTIES

Pumice is a natural silicic foam glass produced by volcanic eruptions. The molten glass foam, upon rapid cooling, trapped the steam and volcanic gases that caused it to remain extremely porous and vesicular in structure. Pumice is found in the form of large lumps several cubic feet in volume and also in grains only a few millimeters in diameter. Chemically, pumicite is of the same range of composition as pumice. The distinction between pumice and pumicite is one of particle size; the coarser materials are pumice; the fine particles, an appreciable percentage of which is in the range of 100 to 325-mesh or finer, are pumicite.

If the erupting volcano ejects a silicic lava containing much gas and water vapor, the sudden release of pressure tends to free the gas. The viscosity of the lava, its rate of cooling and the amount of gas evolved, all have part in determining the degree of expansion of the glassy particles and the fineness of the vesicle. If the lava is of the correct viscosity and there is not too much gas, a pumice may be formed. Large amounts of gas may cause complete disruption into pumicite.³⁰

In 1916, Barbour gave the name "pumicite" to the volcanic ash of Nebraska and since then the name has been widely used in industrial circles for the finer-grained commercial varieties.

The glass of pumice and pumicite is transparent and colorless. It

* Research Engineer, Armour Chemical Division, Armour and Co., Chicago, Illinois.

has a hardness of 5.5 to 6 and a density of about 2.5. Lump and granular pumice is white to gray, or light tan, in color. Its porosity (about $\frac{2}{3}$ of the volume) and glassy composition make it very desirable commercially as a construction aggregate as well as an abrasive. Because of its sealed porosity, pumice is light in weight—one cubic yard in pebble form weighs between 825 and 900 lb—as compared with ordinary sand and gravel, which weighs about 2600 lb per cubic yard. The dead-air cells in pumice give it excellent insulating properties against heat, cold, and sound. The glassy composition makes it practically fireproof. It fuses at about 2450°F.

Perlite is one variety of obsidian, characterized by a perlitic or spherulitic texture, a waxy to pearly luster, a perlitic, splintery, or columnar fracture, and the presence of a relatively large amount, 2 to 5 pct, of chemically combined water. The specific gravity for these acidic glasses all range between 2.3 and 2.5. Silica plus alumina is generally over 80 pct; and combined water 0.1 to 5 pct. Range of color is gray to red to black, and luster is pearly to glassy.

Perlite is expanded by heating the crushed particles very quickly to the softening point, which varies according to the chemical composition within the range 800° to 2200°F. The average is about 1700°F. The combined water present is converted to steam, which expands and forms bubbles within the softened particle.

Expanded perlite may be regarded as a synthetic pumice, which has an advantage over the natural pumice because, through close control of time and temperature of calcination, its properties may be regulated to meet exacting specifications of grain size and porosity.

It can be produced in a form that weighs only 2 to 5 lb per cubic foot with a *K* factor of less than 0.20. Commercial expanded perlite weighs 12 to 14 lb per cubic foot. It is produced either in aggregate size or as closely sized sealed spheroids of foam glass.

DISTRIBUTION OF DEPOSITS

United States—Until recently the greater part of the pumicite production of the United States has been from the deposits of Nebraska and Kansas. At the present time, the trend is toward the production of pumice especially prepared for concrete aggregate. Idaho, California, New Mexico, and Arizona are taking the lead. In California alone, in 1946, more than 20 mines were operating in the following counties: Madera, Siskiyou, Inyo, Modoc, Contra Costa, Mono, Napa, Calaveras, and Kern.

The principal producing area for pumice is near Grants, Valencia County, New Mexico. Other counties in New Mexico with commercial pumice deposits are: Sandoval, Rio Arriba, and Socorro. It is produced also in areas around Klamath Falls, Oregon, and Laws, California.

California, Idaho, Kansas, Nebraska, New Mexico, Oklahoma, Oregon, Texas and Washington report production of pumice or pumicite.

Western perlite occurrences of potential importance are: Superior District, Greenlee County; Yucca, Maricopa County near Aquila, in Arizona; Freemont County at the north end of Ruby Mountains, Colorado; Grant County near Separ, Socorro County near Socorro, New Mexico; Goodsprings district, Searchlight hills, Nevada, and Wasco County, in Frieda district, Oregon.

Canada—Extensive beds of pumicite occur in Saskatchewan and British Columbia. Perlite also occurs in British Columbia.

Italy—Pumice has been worked for many centuries on Lipari, one of the Aeolian Islands off the northeast tip of Sicily.

POLITICAL AND COMMERCIAL CONTROL

The domestic industry is controlled by United States capital. The chief foreign deposits, those of the Lipari Islands, are controlled by Italian interests.

PRODUCTION AND CONSUMPTION

Production of pumice and pumicite in the United States has climbed steadily from about 25,000 short tons in 1920 to 57,000 in 1930; 82,407 in 1940; 157,011 in 1945; 319,883 in 1946; and an all-time high of 442,552 tons, valued at \$2,021,880, in 1947. This sharp upward trend is due principally to its phenomenal growth in use as concrete aggregate in the West. Production of building blocks on a scale that will require 1000 tons of pumice aggregate per day is contemplated.

Italian pumice imports are estimated at 8,000 to 10,000 tons per year. These include three grades: (1) crude lump; (2) sun dried, and (3) prime quality pumice.

PROSPECTING AND EXPLORATION

Many of the deposits of the Rocky Mountain and Pacific Coast states are not covered by overburden, therefore prospecting has not been difficult. Because of the regularity of bedding of the deposits interbedded with other sediments, large tonnages could be blocked out with little expense. The pumicite deposits of Kansas and Nebraska, however, are covered generally by loess or alluvium and are irregular in shape and thickness. In some deposits, exploration is carried on by hand auger holes put down at the intersection of a 50-ft grid, and rather accurate estimates of quality and quantity may be made.

MINING METHODS

Pumice and pumicite are mined both by surface excavations and underground methods, but for operations handling a large tonnage, open-pit methods generally have been adopted. For open-pit mining, the

overburden usually is removed by power shovels. In some operations a thin layer of overburden is left to protect the underlying pumicite until it is mined. Drag scrapers or conventional power shovels are used in mining and quarry haulage usually is by trucks. Explosives may be used to loosen the more compact rock. Deposits in the Rocky Mountain and Pacific Coast states are worked in a variety of ways, depending upon their mode of occurrence. Those with little overburden are stripped and worked by opencuts; the bedded deposits in thick sedimentary formations are worked by systems of tunnels and drifts.

In the early days of pumice mining, large rooms were mined out, but, since some pumice deposits are subject to air slaking, this method is considered dangerous and is not often practiced.

Perlite is mined by accepted open-pit quarry methods. Drilling and blasting methods for quarrying the ore are developed to produce a minimum of oversize to the crushing plant.

PREPARATION FOR MARKET

Pumice is screened, sized, and blended to meet the various specifications of the American Society for Testing Materials for aggregate. The preparation plant for aggregate is relatively simple. The pumicite is dried, screened, and bagged. Some grades for more specialized uses require disintegration or pulverizing to produce a product of which 98.8 pct will pass 325-mesh.

Lump pumice and high-quality ground pumice-stone products for abrasives require a much more complicated preparation system, involving the use of both wet and dry processes.

Perlite is crushed, ground, and closely sized. Control of the particle size and mesh range are very desirable, since they control the physical characteristics of the expanded product. Several types of horizontal and vertical furnaces have been developed to expand the perlite to synthetic pumice. The furnace design is subject to much controversy but scientific data are now being made available through research projects that are crystallizing random thoughts to an exact science. The type of furnace is greatly influenced by the type of product to be made.

TESTS AND SPECIFICATIONS

Tests and specifications for the products of pumice, pumicite, and perlite are confined generally to particle-size distribution, moisture, bulk specific gravity, absorption and the *K* factor or insulating value.

Specifications for utilizing light-weight aggregates have been sadly lacking until recently and have been subject to the whims of the operators or of the buyer and the nature of each deposit.

More attention is paid now to the specifications that are the result of the cooperative research efforts of the producers, State universities

and the various governmental agencies interested in light-weight products. Adequate tests and specifications for building blocks, concrete, monolithic housing units, and other purposes are included in several recent publications.^{7,8,16,35} Producers of abrasive pumice stone are subjected to very rigid specifications.^{16,31}

MARKETING AND USES

Italian pumice is the chief competitor of our domestic producers of lump pumice and sized ground-pumice products. This is especially true in the east coast areas, which are not favored with local deposits of pumice, pumicite, or perlite.

Freight costs of pumice products from the Southwest are less favorable than present ocean rates of \$11 per thousand kilos for Italian pumice.

Domestic producers must also compete with the generally lower labor costs of European countries. Italian pumice enters the United States with an import duty of $\frac{1}{10}\phi$ per pound for crude lump, $\frac{1}{10}\phi$ to $\frac{1}{4}\phi$ per pound for various grades of sun-dried material and $\frac{3}{4}\phi$ per pound for prime or first quality pumice.

Buyer resistance to domestic products is being satisfactorily overcome through the establishment of the dependability of the domestic supply and the furnishing of high-grade materials that will meet exacting specifications.

Use of pumice for concrete aggregate and building block is governed somewhat by transportation costs but, even so, other advantages are rapidly developing eastern markets for western pumice aggregate.

Because of its specialized uses, the market for pumicite is governed more by its purity and physical properties than by transportation cost.

Commercial production of perlite in the United States began in 1946 and sales in 1947 reached 10,810 short tons. The producing states were Arizona, Nevada, California, and Oregon. It is a rapidly growing industry, and, although production is centered in the far western states, the market area may be extended greatly by establishing expanding furnaces in strategic locations, thus overcoming the difficulty of shipping a bulky product.

The principal use of pumicite is for concrete aggregate, and its use as an admixture in cement for concrete is attaining increasing importance. These uses have made extraordinary gains during recent years. In 1947, the quantity so used was 60 pct greater than in 1946. The quantity employed for these uses in 1947 was $4\frac{1}{2}$ times as great as that used for abrasive purposes, the second largest use. Other uses include its employment in acoustic and various other plasters, as an insecticide carrier, in insulation products, as paint filler, and as an absorbent.

The growing interest in the use of pumicite as an admixture with

portland cement to make the type known as puzzolan merits special mention. Since construction of the piers of the Golden Gate and Bay bridges in San Francisco Bay, interest in puzzolan-portland cements has been increasing in the United States, because it appears to be definitely established that concrete made with such cements is more resistant to disintegration by sea water and other aggressive waters. Also, there appears to be reason to believe that puzzolan-portland cements are resistant to the reaction between certain kinds of siliceous aggregates and the alkalis present in some measure in all portland cements.

The pumice or pumicite used as a puzzolan with portland cement may be in a raw pulverized state or it may be calcined at a relatively low temperature, below 1800°F, in rotary kilns. A considerable increase in this use is to be expected in the near future. Table 1 shows trends in principal uses during recent years.

TABLE 1—*Pumice and Pumicite Sold or Used by Producers in the United States, by Uses, 1934-1947*

SHORT TONS

Year	Abrasives	Concrete Aggregate and Admixture	Acoustic Plaster	Miscellaneous	Total
1934	50,018	601	1,581	3,969	56,169
1935	51,567	683	2,860	4,890	60,000
1936	52,270	13,959	3,866	2,820	72,915
1937	50,050	13,839	3,641	3,477	71,007
1938	47,951	7,596	7,115	3,080	65,742
1939	52,521	20,719	5,444	10,475	89,159
1940	50,195	22,045	3,712	6,455	82,407
1941	49,031	56,159	4,885	7,235	117,310
1942	54,408	46,163	4,552	21,399	126,522
1943	63,463	13,794	1,617	6,276	85,150
1944	63,927	17,511	938	6,381	88,757
1945	71,011	72,901	3,693	9,406	157,011
1946	54,454	248,247	4,342	12,840	319,883
1947	31,066	397,223	5,427	8,836	442,552

PRICE HISTORY

The price for Italian pumice in 1936 was subjected to market control and diminishing returns. Approximate 1947 prices were:

1. \$9 a thousand kilos for crude natural pumice stone "Pezame grade."
2. \$12 to \$18 per thousand kilos for crude sun-dried natural pumice.
3. \$19 to \$40 per thousand kilos f.o.b. shipping point for prime or first quality pumice classified as wholly or partly manufactured.

These prices were subject to duty ranging from $\frac{1}{10}\phi$ to $\frac{3}{4}\phi$ per pound. In 1936, prevailing prices for select lump pumice f.o.b. New York were

5¢ to 7½¢ per pound and for ground pumice, 2½¢ to 4½¢ per pound. Market quotations for 1947 varied little from these figures, in spite of higher production costs.

The value of pumice and pumicite produced in the United States increased from \$2.94 a short ton in 1920 to \$5.91 in 1930, decreased to \$3.69 in 1934 and rose to \$4.14 in 1935. In 1940 and 1945, the average price remained at approximately \$6.07 per short ton; in 1946, it was \$4.96, and in 1947, \$4.57.

In California, crude run-of-mine pumice was quoted in 1946 at \$3 per cubic yard f.o.b. car and for ground and screened graded concrete aggregate, \$3.75 per cubic yard. Pumicite for use as insecticide carrier sold for about \$10 to \$15 per ton f.o.b. mill.

Crude perlite is priced at about \$5 per ton f.o.b. car. Prevailing price for processed perlite plaster aggregate is 35¢ per cubic foot in the San Francisco area and 25¢ per cubic foot in the Los Angeles area. Perlite for concrete aggregate ranges from 15¢ to 40¢ per cubic foot. Processed perlite probably will be available at about 15¢ to 35¢ per cubic foot.

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CHAPTER 37

PYROPHYLLITE

BY B. C. BURGESS*

AFTER many years of close and friendly association with talc and soapstone, this orthographically distinguished mineral steps forth in this edition, for the first time in a chapter of its own. Pyr, the Greek for fire, and phyllite, a rock or stone, form its name and at the same time refer to the first recorded use of pyrophyllite as firestones or hearthstones. Another derivation of "phyllite" is from the Greek *phyllites*, "of leaves," alluding to the beautiful white radial crystal aggregates that form when pyrophyllite is heated.

Pyrophyllite used by the Chinese for carving is called agalmatolite, from the Greek *agolma*, meaning an image.

COMPOSITION AND PROPERTIES

Pyrophyllite has previously been grouped with talc because of the close similarity of the minerals in physical and optical properties. They have the same space group; and chemically they are closely related, pyrophyllite being the aluminum silicate $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ and talc the magnesium silicate $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$. Another arrangement of the pyrophyllite formula is generally given as $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ because it expresses the chemical composition as usually determined (alumina 28.3 pct, silica 66.7 pct, water 5.0 pct). Vanderbilt gives pH values of pyrophyllite 5.6 to 8.4.²⁹

Pyrophyllite usually is white, pale green, cream or pale yellow, buff or light gray. It is found in darker shades and other colors principally due to oxidation of contained iron minerals. It is translucent in thin sections.

In hardness it is 1 to 2 in the Mohs scale. Its specific gravity is 2.8 to 2.9. In bulk specific gravity, the powdered mineral ranges from 0.4 to 0.7.

Its luster is pearly to dull; it is infusible in the Bunsen burner flame, slightly affected by aqueous solutions of sodium carbonate and hydrochloric acid. It is decomposed by sulphuric acid, with separation of gelatinous silica. It is characterized chiefly by its micaceous structure and cleavage, its softness and greasy feel. Two other varieties occur

* Consulting Engineer, Monticello, Georgia.

without platy cleavage, one with a radiated needle and granular structure; the other of massive homogeneous structure. Usually, grinding reduces it to flat plates or scales but aggregates of minute foliated plates may be formed.²⁹

DISTRIBUTION OF DEPOSITS

Pyrophyllite is found in metamorphic rocks throughout the world but only in recent years has it assumed commercial importance. The principal production in the United States is in Alamance, Moore, and Randolph Counties in the Central Piedmont area of North Carolina.²⁸ The North Carolina belt actually starts near the Virginia line and extends through South Carolina to Graves' Mountain, Georgia.² Other reported occurrences in the United States are in the South Mountain area of Pennsylvania²⁶ and in San Diego and Mariposa Counties, California.²¹ There are important deposits of pyrophyllite near Manuels, on Conception Bay in Newfoundland,³⁰ also in Nova Scotia near St. Johns and on Vancouver Island.³ It is found also in China, Russia, Sweden, Luxembourg, Belgium, Brazil,⁶ and Japan.¹¹

Pyrophyllite occurs in irregular, lenticular, or bedded deposits, formed, according to Spence,²³ through hydrothermal alteration of original sedimentary or volcanic rocks. Stuckey²⁸ says that the North Carolina deposits were formed through metasomatic replacement of acid tuffs and breccias of both dacitic and rhyolitic composition. He considers them of pre-Cambrian age.

In size, the deposits vary from a few feet in each dimension up to widths of 500 and lengths of 1500 ft. The R. T. Vanderbilt Co.²⁹ reports that the deposit at Robbins has been drilled to a depth of over 500 ft without reaching bottom.

Other minerals found associated with pyrophyllite are quartz, sericite, pyrite, chloritoid, chlorite, feldspar, iron oxides, epidote, zircon, titanite, rutile, zeolites, and apatite.

PRODUCTION AND CONSUMPTION

Pyrophyllite has been mined in North Carolina for many years. Ladoo¹⁴ reports about 10 tons per day being mined in 1922. The best of this was sawed into crayons and the remainder was ground and marketed as talc. Fig 1 shows the estimated annual production and consumption of pyrophyllite from 1922 through 1947. Production figures are not available through the Bureau of Mines but some information may be found in the footnotes to Mineral Industry Surveys.¹⁶

The important developments that have affected consumption of pyrophyllite are:

1. Use of pyrophyllite as firestones and tombstones by early colonial settlers, first mentioned by Emmons in 1856.⁸

2. Mining for crayons, started at Glendon about 1880.
3. Shelton's experiments in 1925, leading to publication of his report in 1929.²²
4. Manufacture of pyrophyllite refractories begun in 1934.
5. Use as a filler in hard rubber products expanded about 1935.
6. Use as an extender for insecticides greatly increased when it was found best "carrier" for DDT, 1942.
7. Use in paints, wallboard and pipe covering developed 1944.

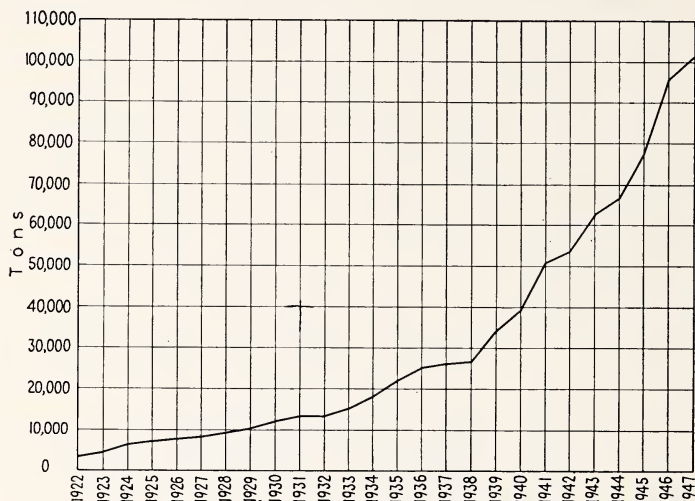


FIG 1—ESTIMATED SALES OF PYROPHYLLITE, 1922–1947.

PROSPECTING AND EXPLORATION

Most of the deposits are of such surface extent that they can hardly escape notice, as when the Gerhardt Brothers farm "wagon wheels brought up a fine, silky, white material."² In other places, the greater resistance of pyrophyllite to weathering has left the deposits as prominent ridges above the surrounding ground.

At first, prospecting and development was principally by shafts and tunnels but as demands for greater quantities have increased and off-color pyrophyllite has been salable, opencuts have been the source of most of the tonnage.

At Robbins, North Carolina (formerly Hemp), the Standard Mineral Co. developed a considerable tonnage of pyrophyllite by diamond drilling before the largest plant in the industry was built there.

MINING METHODS

Following the diamond drilling at the Standard Mineral Company's mine, a 240-ft shaft and some 1200 ft of drifts and raises were driven, then a top-slicing method was used in the stopes, which were from 8 ft to 40 ft wide.¹⁵

One other mine has been conducted as an underground operation for most of its recent life—the one at Glendon, which was first operated as an opencut. As quality requirements became more exacting, a shaft was sunk on a white streak and drifts were run at 30 and 60-ft levels.

Of the two remaining mines, the Gerhardt and Snow Camp, the first was started with a tunnel and raise. The top of the raise was widened into a glory hole and now it is a large open quarry operation. The Snow Camp mine is operated exclusively for refractory products and has been an opencut from the beginning. Its location was selected after several core-drill holes had been put down. Core drilling has been done recently on the Gerhardt mine also to guide the future development.

PREPARATION FOR MARKET

As previously mentioned, the first pyrophyllite mining of commercial importance was for crayons and the waste from this operation

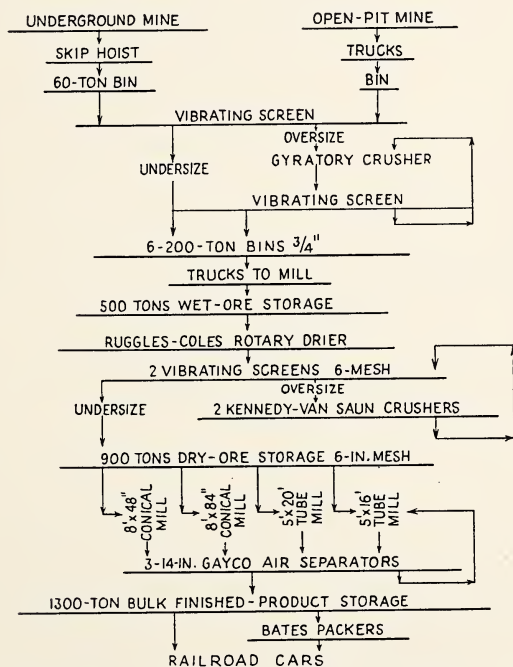


FIG 2—FLOWSHEET, STANDARD MINERAL COMPANY, ROBBINS, NORTH CAROLINA.

was ground as a substitute for talc, but no pyrophyllite crayons have been sawed for 20 years. Now about 95 pct of the market is for fine-ground products; the remaining 5 pct is sold in crude lump form or crushed to pass through a 4-mesh screen for the manufacture of refractory products.

When pyrophyllite was used only as a filler, the simplest method

of pulverizing to the desired fineness was sufficient, but when its use as a ceramic raw material started, quality control became necessary.

Generally speaking, only four grades of pyrophyllite are produced but occasionally one grade is given two or more designations and no effort has been made by the industry to standardize grades. However, each producer claims, with well-deserved pride, that he is able to maintain close uniformity of his own production.

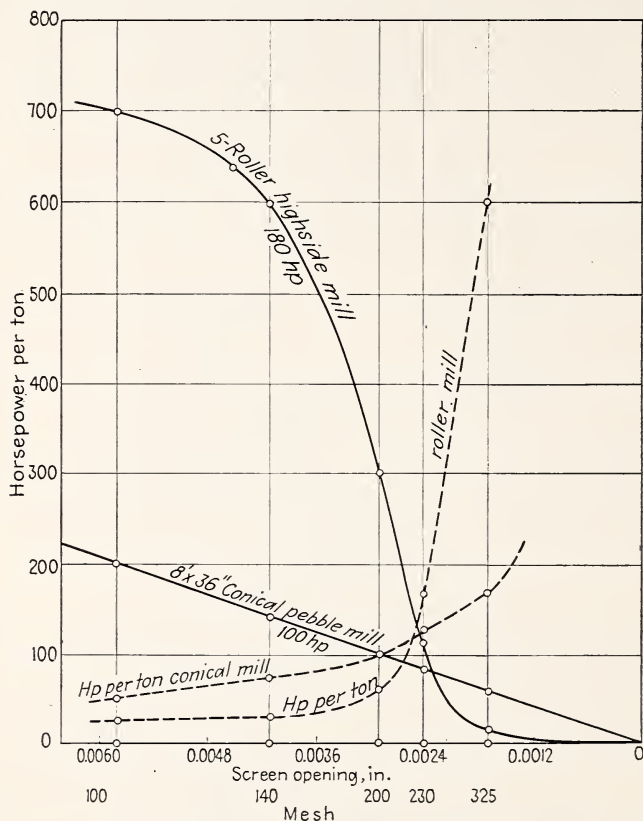


FIG 3—COMPARISON OF CONICAL-MILL AND ROLLER-MILL GRINDING OF PYROPHYLLITE.

The four grades are Pyrax or Standard; No. 3, Refractory or Rubber; Enamel; and HS (high sericite).

The flowsheet of Standard Mineral Co. at Robbins, North Carolina (Fig 2) illustrates the extent to which that company found it desirable to go to control the quality of its products.

Roller mills were used for fine grinding until the ceramic market became important, then the two largest plants were built with conical pebble mills. Fig 3 shows comparative grinding rates of conical mills and roller mills. The efficiency of the roller mill drops off rapidly for grinding finer than 200-mesh and this also has contributed to the increased use of conical mills.

TESTS AND SPECIFICATIONS

For practically all uses, pyrophyllite must be furnished in uniform particle size, mineral content, or both. No uses have developed requiring through-on sizes like those of some mica products. The complete mill product is used, fineness being determined by maximum residue on the screen designating the size; in most cases, fineness classification is the same as for feldspar.²⁵

The need for control of mineral content is illustrated by the analysis of seven samples taken in the Gerhardt mine (Table 1).

TABLE 1—Analysis of Pyrophyllite from Gerhardt Mine

Constituent	Composition, Pct						
	(1) ^a	(2) ^a	(3) ^a	(4) ^a	(5) ^a	(6) ^b	(7) ^c
Silica.....	76.32	73.50	70.26	69.90	69.38	83.34	77.22
Alumina.....	19.80	22.53	24.95	25.13	26.02	13.93	15.95
Iron.....	0.18	0.09	0.08	0.07	0.08	0.13	0.35
Calcium.....	0.14	0.08	0.16	0.16	0.14	0.42	tr
Magnesium.....							
Potash.....	0.27		0.13	0.00	0.00	0.00	3.54
Soda.....	0.07	0.06	0.31	0.08	0.24	0.18	0.93
Loss.....	3.44	3.95	4.32	4.67	4.50	2.20	2.08
	100.22	100.21	100.21	100.01	100.36	100.24	100.07
Pyrophyllite.....	66	79	85	88	89	48	5
Quartz.....	31	21	12	11	9	51	57
Sericite.....	3		3	1	2	1	38

^a Pyrophyllite.

^b Granular quartz.

^c Sericite.

Sericite is an active flux in ceramic products and no pyrophyllite would be acceptable for this important use without close control of this mineral. The ratio of quartz to pyrophyllite is also important. In low-sericite pyrophyllite, this may be determined from the water of crystallization ($20 \times \text{H}_2\text{O} = \text{pyrophyllite content}$). In other cases, a complete chemical and rational analysis is necessary.

MARKETING AND USES

The uses of pyrophyllite are many and varied. Starting out as a hearthstone and tombstone, it next found favor for steelmaking crayons when the supply of talc crayons was low. The search for a wider market for the powder developed an interesting field in ceramics and the next natural field for it was found in refractories. Now it is used also in roofing, cotton cordage, textiles, rubber, soap, paints, cosmetics, bleaching powders, hard rubber, wallboard, welding-rod coatings, and

insecticides. The limit of usefulness has not been reached and may continue to expand.

In Ceramics—Vanderbilt gives formulas (Table 2) for eight ceramic products using pyrophyllite.²⁹

TABLE 2—*Typical Whiteware Bodies Containing Pyrophyllite^a*

Product.....	1	2	3	4	5	6	7	8
Flint.....	10.0		20.0			5.0	8.0	10.0
Feldspar.....		52.0	3.0	35.0	33.0	20.0	33.0	9.0
HS "Pyrax" pyrophyllite....	40.0	16.0	13.0	19.0	22.0	20.0	10.0	27.0
Ky. Tenn. Clay Co. No. 4 ball.	18.0	7.0	16.0	8.0	10.0	20.0	9.0	10.0
Wade No. 5.....							10.0	15.0
No. 12 ball.....				8.0				
Ky. Clay Mining Co. No. 5 ball.....			16.0					
"KCM".....					8.0	15.0	6.0	10.0
"Cherokee" Ga. kaolin.....	18.0		25.0	15.0				
"Peerless" S. C. kaolin.....		10.0			10.0	10.0	10.0	18.0
Edgars E.P.K. Fla. kaolin....		15.0		15.0	10.0	10.0		
Harris "Lunday" N. C. kaolin					7.0		8.0	
Loomis, N. Y. state, talc.....	12.0		6.0					7.0
Whiting.....	2.0		1.0					
Moore and Munger No. 27 Ga.							6.0	

1. Wall-tile body—Cone 1 to 5.
2. Floor-tile body—Cone 9 to 10.
3. Earthenware body—Cone 6 to 8.
4. Dry-pressed insulator body—Cone 11 to 12.
5. Plastic molded insulator body—Cone 10 to 12.
6. Plastic molded insulator body—Cone 11 to 13.
7. Sanitary-ware body—Cone 11 to 12.
8. Artware body—Cone 1 to 3.

^a From Vanderbilt.²⁹

In wall tile, pyrophyllite has had a very important function. Its use permits a good glaze fit and has enabled manufacturers to guarantee their product against delayed crazing.

A special high-alumina product is made for porcelain enamel. The value of pyrophyllite in this product is that it provides a cheaper source of low-iron and titania alumina than is obtainable in kaolins. The pyrophyllite sold for porcelain enamel contains 24 pct alumina and is 85 pct pure pyrophyllite mineral, whereas the standard grade containing only 18 pct alumina is only 67 pct pyrophyllite.

In Refractories—Greaves-Walker⁸ says: "Mixed with refractory bond clays this mineral produces refractories which have remarkable physical qualities. It has a high fusion point, does not shrink under high temperatures, has good resistance to the action of slags which are not

high in iron and, what is very important in a refractory, it does not spall under severe temperature changes."

Paints and Wallboard—The newest field for pyrophyllite is in paints and wallboard and for these it requires the finest grinding. In paint, it acts as a low-priced extender of expensive pigments and because of its platy character has good covering power. In wallboard, fine-ground pyrophyllite has the effect of making the plaster flow more smoothly.

Tonnage—Since no figures have been published, it is difficult to get accurate information on the tonnage produced and used by the different industries. However, estimates from several sources have been averaged in Table 3.

TABLE 3—*Estimated 1947 Pyrophyllite Market*

Industry	Grade	Mesh	Tons
Insecticides.....	No. 3	230	27,000
Hard rubber.....	Rubber	200	24,000
Ceramics.....	Standard	200	9,000
Refractories.....	Refractory	Crude and crushed	5,000
Paint.....	Standard	325	5,000
Roofing.....	No. 3		3,000
Cosmetics.....	Standard	230	3,000
Wallboard.....	Standard	325	3,000
Cordage.....	Standard	200	2,500
Bleaching powder.....	Standard	200	2,000
Textiles.....	Standard	200	1,500
Soap.....	Standard	200	1,000
Rubber.....	Standard	230	500
Miscellaneous.....	Standard	200	17,000
			103,500

PRICE HISTORY

Starting with hearthstones, which the early settler could get just for his own labor, then as a substitute for talc and at present with many expanding uses, pyrophyllite has been and continues to be a low-priced product. Prices in 1943 are given in Table 4.

Since 1943, prices have increased 10 to 15 pct. Demand continues at a high ratio to the capacity of the industry and unless additional competition develops there will no doubt be further increases. Present prices provide only reasonable return on the investment. There is no tariff on pyrophyllite imports.

Pyrophyllite is grouped with clay and kaolin for freight-rate classification. In October 1947, rates constituted 30 to 50 pct of the delivered cost to the average consuming point.

TABLE 4—*Carload Prices per Ton of Pyrophyllite in 1943*

Type	Grade	Price	
Crude.....	Refractory	\$4.00	
Crude.....	Ceramic	5.50	
Crushed.....	Refractory	5.50	
Crushed.....	Ceramic	7.00	
140-mesh.....	Enamel	13.00	
Other Fine Grinding			
Mesh	Rubber	No. 3	Standard
200	\$5.50	\$ 8.00	\$10.00
230	6.50	9.00	11.00
325	8.00	11.00	13.00

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CHAPTER 38

QUARTZ CRYSTAL

BY ROBERT B. McCORMICK*

THE major use for quartz crystal is in the manufacture of radio oscillator plates and telephone resonator and filter crystals. Quartz crystal is also cut and polished as a semiprecious gem stone, particularly in the colored varieties (amethyst, Brazilian topaz, and others), and often is carved into various objects of art. Prisms, wedges, lenses and other optical parts often are made of quartz crystal, usually for special-purpose instruments. Chips and small clear crystals below 100 grams in weight, called "lascas" by the trade, are the raw material for fused quartz products.

HISTORICAL BACKGROUND

The Greeks believed quartz to be permanently frozen water and therefore called it *krustallos*, which, literally translated, means clear ice; but ages before their civilization, prehistoric man had crudely cut and polished crystals for rough charms and ornaments. About 2000 B.C., the Egyptians brought the art of cutting quartz to a high level. While there are earlier examples of crystal art that have great value, working in crystal during that period became a means of artistic and religious expression that has endured through the ages. Art museums and private collections throughout the world contain many priceless pieces. They include findings from the tombs of the earliest Egyptian rulers, as well as magnificent art objects in both clear and colored crystal encrusted with silver, gold, enamel, and precious gems of oriental and European workmanship.

Pierre Curie first measured the piezoelectric effect of quartz, in 1881, by placing a weight on the surface of a quartz crystal and measuring the resulting electrical charge, which he found was proportional to the weight applied. The following year the inverse piezoelectric effect was proved by the Curies. By applying a voltage to a piece of quartz, a measurable physical displacement occurs. The first practical application of this effect was the construction of a bimorph unit to measure voltage by measuring the amount of the displacement of the end of the bimorph.

The piezoelectric properties of quartz crystal remained largely a laboratory curiosity until World War I, when a supersonic device for

* Office of Materials Resources, Munitions Board, Washington, D. C.

the detection of submarines using quartz crystal plates was developed for the French Navy by Professor Langevin. Unfortunately, the instrument was not perfected until after the Armistice but similar units were used extensively in World War II. Professor Cady, of Wesleyan University, first showed that quartz crystal could be used to control the frequency of radio oscillator circuits in 1921, and as a result of his work they were soon being used in radio transmitters. Quartz crystal has since been adopted for accurate frequency control in many electronic devices.

World War II was primarily a war of fast-moving tactical units and, in order to coordinate their movements and keep them supplied, adequate communications under the stress of combat conditions were an absolute necessity. Radio was the obvious answer and our entry into the war was followed immediately by the development and production in great quantity of "walkie-talkies," "handie-talkies," tank, artillery, aircraft, and naval radio sets and other electronic equipment. The answer to simplicity and dependability of operation was the design of crystal-controlled oscillator circuits with a quartz crystal oscillator plate for every transmitting and receiving frequency at which it was desired to operate the equipment. Such crystal control, in effect, meant "push-button" transmitter and receiver tuning, requiring a minimum of personnel training. Some mobile units in the armored forces were supplied with as many as 120 frequency channels, requiring one transmitter crystal and one receiver crystal for each channel as well as a complete set of spares for each radio set. As a result of this demand, quartz crystal, almost overnight, became a strategic material of prime importance.

COMPOSITION AND PROPERTIES

Quartz crystal (chemical composition, SiO_2) is a common mineral, which crystallizes in the hexagonal system. Crystals usually are six-sided prisms terminated by a positive and a negative rhombohedron, often about equally developed and resembling a hexagonal bipyramid. Prism faces usually are horizontally striated and twinning is common.

Quartz crystal has no cleavage but has a conchoidal fracture. It is brittle, transparent to translucent, has a vitreous luster, hardness of 7 (Mohs' scale), and a specific gravity of 2.65. Crystals exhibit pyroelectric and piezoelectric properties and commonly are colorless or white although they may be yellow, pink, red, amethystine, green, blue, brown or black. Indices of refraction are: $N_o = 1.544$, $N_e = 1.553$.

DISTRIBUTION AND OCCURRENCE

Small deposits of quartz crystal are known to exist in the United States, particularly in Arkansas, California, Virginia, North Carolina, and New York. Mines in Arkansas and California were worked intensively during the war with Government aid but only small quantities

of radio-grade crystal were produced. Prospecting in these and other areas was notably unproductive and the United States is dependent on foreign sources for supplies of this strategic mineral.

Although small deposits of quartz crystal have been reported from Australia, Guatemala, Colombia, Madagascar and the Soviet Union, Brazil has a virtual monopoly on the world's resources. The important Brazilian quartz crystal deposits are principally in the states of Bahia, Goiaz, and Minas Gerais, and smaller producing areas are in Espirito Santo, Para, and elsewhere. The deposits, in the main, are spread over wide areas.

Brazilian quartz crystal occurs in veins, pegmatites and residual deposits of various types. The extremely small proportion of usable crystal recovered per ton of earth moved is the most striking feature of all the deposits. Tremendous quantities of milky bull quartz must be mined in order to recover a few pounds of clear, usable crystal. Many hundreds of mines or diggings, very few of which are underground operations, were required to produce sufficient quartz crystal for the Allied Nations in World War II. Estimates made during the war period indicate that not more than 10 or 12 mines in Brazil produced a ton of usable crystal per month for any length of time. Most diggings apparently produced considerably less.

The occurrence of quartz crystal in Brazil is described by Johnston and Butler³ as follows:

"The veins (including composite lodes, pipes and pockets, stock-works, and bedded veins) consist principally of milky comb quartz, usually completely intergrown, and of variable but relatively coarse texture. The general impression is that the milky quartz individuals are ten centimeters or more in length, but in many places crystal outlines cannot be recognized within the mass of the bull quartz. . . . Typically, the veins display structure wherein the comb quartz crystals have grown inwards from the walls toward the centers of the veins. Vugs, lined with well-formed crystals, are usually abundant. Occasional crystals in these vugs have clear, transparent prisms or terminations which furnish the material suited for the manufacture of oscillators. Large clear crystals are relatively rare, whereas small clear prisms are very common.

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"Pegmatites yield some quartz, but in comparison with the yield of quartz veins, the quantity is small.

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"Residual (eluvial) quartz deposits occur through the crystal-producing regions of Brazil. They grade on the one hand into colluvial and alluvial deposits and on the other into primary deposits in place or es-

entially so. Some of the best examples of residual deposits are found at Cristalina, Goiaz, where narrow cappings of residual quartz fragments . . . extend for a kilometer or more along fold axes with pockets and veins of quartz crystal in the underlying sandstone. Here, the primary quartz deposits are located by means of the residual quartz blanket . . . The residual blanket grades downward into primary quartz, and many fragile vug structures lie essentially undisturbed in deeply weathered sandstone. Similar residual blankets yielded much of the early production . . . and were generally responsible for the discovery of individual quartz deposits throughout Brazil.

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"Where primary quartz, in either veins or pegmatites, crops out on steep hillsides, the material loosened by weathering slides down the hill forming hillside creep (colluvial) deposits. The material is an unstratified mixture of partially decomposed rock and clay containing both complete crystals and fragments of quartz. Generally the quartz is frosted, and the corners are more or less rounded, depending on the distance the material has travelled.

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"Water-laid (alluvial) deposits occur throughout the crystal-producing areas, but so far as is now known they are best represented in Central Minas Gerais and in Espirito Santo. In general, quartz from stream deposits has a higher ratio of usable material than that from the primary deposits because the shock of colliding fragments during stream transport has tended to break crystals along actual or incipient fractures so that many of those that remain unbroken are sound. The quartz crystals and fragments become rounded (*rolados*) and frosted so that 'windows' must be chipped in them for examination in the field."

POLITICAL AND COMMERCIAL CONTROL

The political and commercial control of the production and trade in quartz crystal is the complete monopoly of the Brazilian Government. An official table (*tabella*) is periodically published, which establishes the specifications of crystal for export and sets minimum export prices for the various classifications. Export taxes on an ad valorem basis are assessed on all quartz crystal shipments after thorough inspection by Brazilian customs officials.

Quartz crystal imports into the United States are not dutiable, since the material is on the "free list" of the Tariff Act of 1930.

MINING METHODS AND PREPARATION FOR MARKET

With regard to the mining methods and preparation of crystal for market in Brazil, Johnston and Butler³ say:

"The major portion of quartz crystal produced in Brazil has been mined by individuals or by small groups working in partnership. The typical miner is called a *garimpeiro*; he is an individualist and leads a primitive, nomadic existence. His activities are entirely influenced by personal economic conditions. He may abandon the pit in which he is digging quartz in order to wash gold or diamonds, or, if food is temporarily scarce, may take to raising the staple of his existence, rice and beans.

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"The classical method in Brazil for mining quartz crystal is by means of pits. In a single district, or *garimpo*, hundreds of small pits, each worked by one or two miners, are spread throughout the crystal-bearing ground; many more exploratory pits may be around the margins. If it is possible for the pits to follow minable ground to depth, benches are left at suitable intervals, which serve as shovel steps. In a few places, primitive hoisting equipment has been constructed to eliminate the necessity of benches. In a few large deposits, benched open cuts were evolved, and in some of these more than a dozen shovel steps were present—often as many in the dump material as in the pit. Tools are picks, shovels, hammers, moils, and wedges. One miner with a pick and one with a shovel would be engaged in actual digging at the bottom of the pit or cut, and each shovel step would have its individual shoveler hoisting material up the face and over the dump. . . . In many places work comes to a standstill during the rainy season when pit bottoms become flooded. Common dewatering practice is by means of bailing with gasoline tins, passing the tins from man to man either up a chicken ladder or from step to step.

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"During the war improved mining methods were installed at a number of mines in Minas Gerais and Bahia. The methods and machines employed were relatively simple, and the purpose was to increase the rate of production and realize greater recovery. Scrapers and bulldozers cleared overburden and removed old dumps which could not have been handled economically by hand; compressors, clay diggers, machine drills, mine cars, buckets, and hoists increased the rate of extraction; and pumps permitted operation during the rainy season.

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"The cost of mining crystal ranges from Cr\$40.00 to Cr\$200.00 (\$2 to \$10) per kilogram. This size distribution and quality of the mine-clean product vary from mine to mine and particularly from district to district. Mines producing an undue proportion of small sizes or material known to be low in grade receive a relatively low price for their prod-

uct, but, on the whole, an average of approximately Cr\$100.00 per kilogram for mine-clean crystal was sustained in the mining district during the past 2 years (1943-44). The average value shown on export invoices during 1944 was Cr\$250.00 per kilogram of crystal.

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"The production of a garimpeiro is sold to either a travelling buyer or local businessman such as a storekeeper. The miner washes the stones which he finds, views them in daylight and trims off the obvious imperfections with a small chipping hammer. The material is then considered 'mine clean' and as such begins its travels to the ultimate market. The first buyer collects a considerable quantity of material and then may sell it locally, in a near-by town, or bring it to a port; but in most instances the merchandise passes through five or six hands before exportation. At any stage the temporary owner may clean the quartz by further trimming and eliminate unsuited material through inspection with polariscope or arc lamp in order to obtain a higher-quality, higher-priced product. Large stones which are low grade upon examination, are trimmed so as to produce a smaller quantity of higher-grade material. The final product for export is thus only part of the mine production. It is estimated that approximately half of mine-clean quartz is suitable for export, although the ratio will vary according to the individual deposit and the skill and commercial relationships of the producers and dealers involved."

GRADING AND MARKETING

Prior to World War II, the grading of quartz crystal in Brazil by the exporter was, in most cases, a haphazard operation combining the sorting of crystals by weight classes and an estimation of the "usability" of each individual crystal by visual inspection for inclusions, bubbles, and other defects, and for surficial evidences of optical or electrical twinning. The introduction of the polarizing oil tank for the determination of optical twinning and of the arc-lamp beam to inspect crystals for inclusions occurred just before the entry of the United States into the war. These accessories were in general use by exporters in Brazil before the conflict ended.

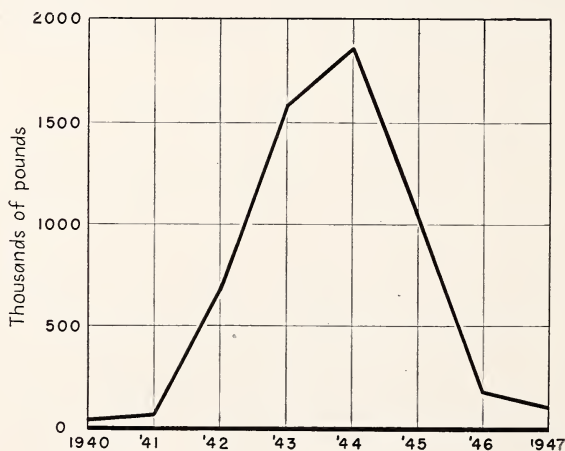
Four standard grades of quality are used by the trade, designated as A, B, C, and D, depending on the estimated quantity of usable material contained in each crystal. In addition to the usability classifications, quartz crystals are sorted into 11 weight classes: 100-200, 200-300, 300-500, 500-700, 700-1000, 1000-2000, 2000-3000, 3000-5000, 5000-7000, 7000-10,000 and above 10,000 grams. Crystals may also be sorted on the basis of the presence or absence of natural crystal faces. As a result of the "usability" weight and "faced-unfaced" classifications, there

are 88 possible classes that must be taken into consideration when quartz is graded. Because of the personal element involved in the estimation of the amount of optical twinning in using the polarizing oil bath, the percentage usability of a crystal is a most difficult determination and has been the source of much disagreement and misunderstanding.

Shipment of quartz crystal from Brazil is made in wooden boxes about the size of an orange crate. Each box contains about 100 lb of crystal. During World War II, because of the urgency of the situation, most American consumers purchased quartz crystal sight unseen from private importers or the Government (Government quartz crystal was graded by the National Bureau of Standards before sale to oscillator manufacturers). In peacetime, however, most purchases are made on the basis of an inspection of the material by the purchaser at the importer's place of business or at the purchaser's plant.

CONSUMPTION AND PRICES

No separate statistics are available, but consumption of quartz crystal in the United States prior to 1939 probably was less than 30,000 lb a year. During the war, however, consumption rose to a peak of almost 1,900,000 lb of radio-grade material (1944). Fig 1 shows the annual consumption of radio-grade crystal for the period 1940 to 1947.



SOURCE: Minerals Year Book, U.S. Bureau of Mines.

FIG 1—ANNUAL CONSUMPTION OF RADIO-GRADE CRYSTAL, 1940–1947.

The general price trend of quartz crystal in Brazil has been steadily upward since 1940 with little or no downward readjustment since 1945. Because of the very numerous sizes and qualities into which it is graded, American retail prices for crystal may range all the way from about \$2 per pound for 100 to 200-gram crystals up to as high as \$50 or \$60 per pound for crystals of good quality weighing more than 10,000 grams.

each. It is estimated that the average retail price for radio-grade quartz crystal in the United States was about \$7 per pound in 1944.

SUBSTITUTES

Because of the strategic nature of quartz crystal, the importance of substitute materials during the war years was not overlooked. Programs of an experimental nature were instituted by interested companies and agencies of the Government in an attempt to find a natural or synthetic substitute for quartz crystal. Research in the production of quartz crystal by chemical synthesis was also begun and is still continuing.

A satisfactory substitute (ethylene-diamine-tartrate) for quartz crystal telephone resonators and filters has been developed and is being used extensively by the Bell System in long-distance telephone circuits. This material, however, is not suited to the production of the high-frequency oscillator plates and supersonic antisubmarine devices used by the armed services.

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CHAPTER 39

REFRACTORIES

BY PAUL M. TYLER* AND R. P. HEUER†

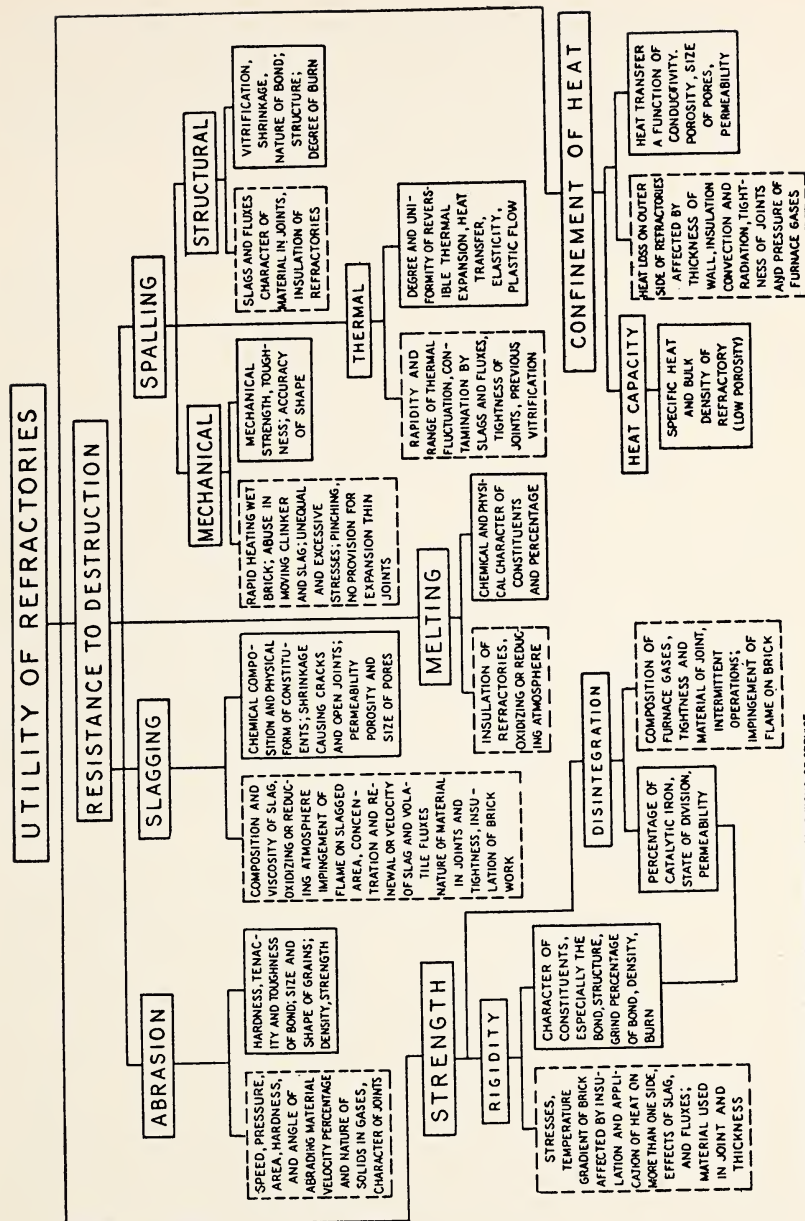
THE literature on refractories, although fairly extensive, is so scattered through books and periodicals as to be difficult of access to the general reader and most of the individual papers serve merely to illuminate some particular phase of the industry. Two general treatises by American authors^{8,16} are available, also the somewhat older works by a well-known British authority,^{12,13} but these make their appeal to the technically minded ceramic engineer. Another small group of publications deals with the use of refractories, mainly in the iron and steel industry.^{1,3,5,6,11,15} Raw materials utilized by the refractories industry have been covered by sundry books and articles. For the relatively non-technical reader and economist, however, there appears to be no single review that purports to describe the industry as a whole.

Furnace linings and other products that are classed as "refractories" are designed primarily to withstand high temperatures but this important property is by no means the only requirement; a suitable refractory material must likewise withstand slagging (chemical action), abrasion (physical wear), and spalling, as well as the various other stresses and physical phenomena induced by heat, of which softening or incipient melting is only one phase. Nevertheless, subject to these highly practical considerations, the definition of a refractory material is based upon temperature resistance. Broadly speaking, any material that shows obvious signs of fusion after being heated slowly to 1500°C (2732°F) cannot be classified as a refractory material.

The characteristic properties and requirements of refractory materials are conveniently summarized in Fig 1, prepared on the American Refractories Institute Fellowship at Mellon Institute, Pittsburgh, Pennsylvania. Most of the factors of service and properties of refractories given in this chart are interdependent and are greatly affected in degree by the functions of temperature and time. The factors in the chart are believed to cover the commoner questions.

* Consulting Mineral Technologist and Economist, Kensington, Maryland.

† Vice President in Charge of Research, General Refractories Co., Philadelphia, Pennsylvania.



NOTE. FACTORS ENCLOSED IN BROKEN BOXES REPRESENT CONDITIONS OF SERVICE WHILE THOSE IN SOLID BOXES REFER TO PROPERTIES OF REFRACTORIES

FIG 1—CHART FOR DETERMINING UTILITY OF REFRACTORIES UNDER DIFFERENT CONDITIONS OF SERVICE.

CLASSIFICATION OF REFRACTORIES CONSUMERS

Various estimates have been made as to the relative importance of different industries as consumers of refractories and the following is perhaps as good an approximation as can be made without getting average figures of actual sales over a period of years.

Estimated Distribution of Sales of Refractories

INDUSTRY	PERCENTAGE OF	INDUSTRY	PERCENTAGE OF
	TOTAL SALES		TOTAL SALES
Iron and steel.....	63	Basic and silicate	
Public utilities	14	(ceramic, etc.)	9
Nonferrous metals.....	6	Chemical process	4
		Miscellaneous	4

The iron and steel industry is the leading user of refractories. Refractory materials are required for the construction of blast furnaces and hot-blast stoves in the production of pig iron; of open-hearth, electric, and other furnaces used in the melting and refining of steel; soaking pits, reheating furnaces, and mill furnaces for the fabrication of the various steel products; boilers for the generation of steam; coke ovens; gas producers; and a host of other auxiliary apparatus.

The public utilities and power-generating stations form the second largest consuming group. Included in this category may be considered the large central-station electric plants, individual steam-boiler plants, plants for the manufacture of city gas, railway locomotives, incinerators, sewage-disposal plants, and others.

The iron and steel industry, public utilities, and other power production thus account for more than 70 pct of the entire consumption of refractories. The remainder is divided among a great variety of consumers. Prominent among them may be considered the nonferrous metal industry, which includes the smelting and refining of copper, nickel, lead, zinc, brass and other metals or alloys. Of considerable importance are the quantities used in the construction of the vertical shaft kilns and rotary kilns used for burning cement and lime. The production of glass requires refractory materials for the construction of furnaces used in the melting of glass and in the annealing and working of finished glass products. The ceramic trades also include the production of china and porcelain, sewer pipe and building brick. Oil refining requires the construction of stills and auxiliary apparatus, which consume important amounts of refractories products. The manufacture of chemicals, the refining of salt and sugar, the manufacture of wood pulp and paper, all occasion the consumption of refractories.

In many industries the efficiency of the processes and the capacity of the equipment, together with its useful life, are circumscribed by the

ability of refractories to perform their allotted jobs. It follows that progress in the production of suitable refractories at reasonable cost is of national concern insofar as it contributes to the betterment of many other products and reduces operating costs in our key industries.

TYPICAL REFRACTORIES PRODUCTS

The typical refractory product is supplied in the form of brick and preformed shapes. Standard bricks are 9 by $4\frac{1}{2}$ by $2\frac{1}{2}$ in. but there are numerous other so-called standard shapes, which are used in all types of construction and which, consequently, are stocked by most manufacturers. These include straight brick of different dimensions (small 9-in., split, soap and checker brick), sundry wedge, arch, skew, key, jamb, bung-arch, and neck shapes. The size tolerance on standard shapes and straight brick (American Society for Testing Materials) is 2 pct, plus or minus, on all dimensions. Silica standard shapes are virtually the same as firebrick, while magnesite, chrome and special or high-priced refractories are available in a more limited range of sizes and shapes. Among special shapes are various tile, segmental blocks for lining cylindrical kilns and cupolas, glass-tank blocks, coke-oven shapes, checker brick, burner tiles, boiler shapes, and so forth.

Saggers and other forms of kiln furniture employed in the ceramic industry to protect or support ware while it is being burned account for a considerable volume of refractory shapes. Muffles of various sizes also are furnished for use in the manufacture of enamelware and in many kinds of small furnaces for commercial heat-treating and laboratory work. Gas retorts and zinc-smelting retorts are refractory products of some importance. Crucibles are made in many shapes and sizes and from a great variety of materials; graphite-clay mixtures (6 to 50 pct graphite) used for melting metals are the leading products in this class, although other refractory mixtures, including silicon carbide, alumina, zirconia and beryllia, are sometimes used. Glass pots are essentially fire-clay crucibles of medium or large size used in glassmaking. Among various special refractory products may be mentioned stoppers, tubes, and such highly specialized items as laboratory ware, spark-plug cores, and other heat-resistant porcelain products.

Ordinary siliceous sand, grain magnesite, dolomite, chrome ore, and certain other materials are purchased in bulk or loose condition and rammed into place or spread evenly over the bottoms of furnaces. Plastic mixtures of firebrick, chrome ore and sillimanite shipped in drums or cardboard cartons are employed for monolithic structures, patching or general repair work, and various refractory cements and mortars are available for use in making joints and for putting a protective coating on brick structure.

PRINCIPAL VARIETIES OF REFRACTORIES

The common refractories may be classified under the group headings Fire Clay, High-alumina, Silica, Magnesite, and Chrome. Fire-clay refractories are the least expensive and constitute by far the largest tonnage. Silica refractories form the next largest group, their average price being somewhat higher than that of fire-clay products. High-alumina brick, chrome brick, and magnesite brick follow in order of increasing cost. Still more expensive are the refractories that include the synthetic materials, such as silicon carbide and fused mullite, also fused alumina, fused magnesia, and other electric-furnace products, together with the special refractories made from comparatively expensive raw

TABLE 1—*Properties of Refractory Materials*

Material	Formula	Melting Point		Sources
		Deg C	Deg F	
Silica (cristobalite)....	SiO ₂	1728	3142	Quartzite, sand
Kaolinite.....	Al ₂ O ₃ .2SiO ₂ .2H ₂ O	1785	3245	Fire clay, kaolin
Mullite.....	3Al ₂ O ₃ .2SiO ₂	1830 ^a	3326 ^a	Kyanite, sillimanite, andalusite
Alumina.....	Al ₂ O ₃	2040	3704	Bauxite, diaspore
Chrome ore.....	(Fe,Mg)O.(Cr,Al,Fe) ₂ O ₃	Above 1970	Above 3578	Chrome ore
Spinel.....	MgO.Al ₂ O ₃	2135	3875	Synthetic (electric furnace)
Silicon carbide.....	SiC	Dissociates above 2500	Dissociates above 4532	Synthetic (electric furnace)
Beryllia.....	BeO	2510	4550	Beryl
Yttria.....	Y ₂ O ₃	2410	4370	Monazite sands
Dolomite (burnt)....	CaO.MgO	2500	4532	Dolomite
Zircon.....	ZrO ₂ .SiO ₂	2550	4622	Zircon sands
Lime.....	CaO	2570	4658	Limestone
Graphite.....	C	^b	^b	Carbon
Magnesia.....	MgO	2800	5072	Magnesite, sea water
Thoria.....	ThO ₂	3050	5522	Monazite sands, thorite, thorianite

^a Dissociates into corundum (Al₂O₃) and liquid. Entirely liquid at approximately 1910°C (3470°F).

^b Carbon, in all forms, volatilizes without melting at ordinary pressures.

materials such as zirconia, beryllia and thoria. As the cost of production of these refractories rises, their utility becomes smaller and smaller, until certain super-refractories, like thoria, are so expensive that they can be used only in laboratory or similar small-scale work.

Fire-clay Brick

The majority of refractories used today are classed as high-heat-duty fire-clay brick. These usually are made of a combination of flint clays that are refractory but not plastic and highly plastic clays that are only moderately refractory. In the United States these raw materials come mainly from Pennsylvania, Kentucky and Missouri, while

less extensive deposits are worked in Illinois, Ohio, Colorado, Texas, Utah, New Jersey, Washington, Maryland and California. Kaolins, immense deposits of which are found in Georgia, are also employed in the manufacture of high-heat-duty firebrick.

Fire-clay brick are classified by the American Society for Testing Materials in specification C27 as follows:

High Duty: pyrometric cone equivalent not lower than cone 31–32 or not more than 1.5 pct deformation in the 2460°F load test. *Intermediate Duty*: not lower than cone 29 or not more than 3 pct deformation in the 2460°F load test. *Low Duty*: not lower than cone 19. *Superduty*: not more than 1 pct linear shrinkage in the permanent linear change test (2912°F and not more than 4 pct loss in the panel spalling test (preheated at 3000°F). The pyrometric cone equivalent shall not be less than cone 33.

High-duty brick are used in lining blast furnaces and hot-blast stoves, checker chambers for open-hearth steel furnaces, steam-boiler settings, oil stills, and a great variety of miscellaneous furnaces. Where service conditions require brick superior to high-duty, the superduty are substituted. Typical examples are high-temperature boiler installations and top courses of checkers in blast-furnace hot-blast stoves. For other special conditions, an entire range of high-alumina refractories has been developed. Typical chemical compositions of the more important types are given in Table 2.

High-alumina brick are manufactured from combinations of plastic and flint clays, burleys and diaspores, mainly from Missouri, and imported bauxite. The 50 pct alumina brick are used in relatively small

TABLE 2—Typical Analyses of Fire-clay and High-alumina Brick

Component	Composition, Pct							
	Fire-clay Brick			Super duty	High-alumina Brick			
	High-duty ^a				50 Pct	60 Pct	70 Pct	80 Pct
	1	2	3					
Silica.....	76.6	62.5	50.0	53.0	44.68	31.92	23.20	13.36
Iron oxide.....	1.1	1.5	2.8	1.1	1.41	1.56	1.25	0.86
Alumina.....	19.7	33.6	42.3	42.9	50.37	61.04	71.25	80.21
Titania.....	1.7	1.6	2.5	2.1	2.46	3.24	2.70	3.93
Lime.....	0.1	0.1	0.1	0.3	0.37	0.24	0.27	0.10
Magnesia.....	0.1	0.1	0.7	0.4	0.36	0.35	0.28	0.36
Alkalies.....	<i>b</i>	0.7	2.0	0.5	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>

^a 1, Jersey semisilica; 2, Texas; 3, Pennsylvania.

^b Not determined.

quantities, principally where temperatures are too high for high-duty or superduty. The 60 pct alumina brick are more widely used than the 50 pct, their principal use being in high-temperature boilers and certain lime kilns. The 70 pct are most widely used; they are employed chiefly in lime and portland cement kilns and in lead smelting and refining furnaces. The 80 pct alumina brick are used in only very limited quantities.

Silica Refractories

One of the earliest types of refractory material was natural siliceous rock, rough-hewn into blocks. Sandstone blocks are still used and highly siliceous "mica schist" finds some application as furnace lining. Common sand also is still used to some extent in its natural state for furnace bottoms. Diatomite is another natural material, used mainly in furnaces for its heat-insulating properties and low density; also because it is refractory.

The common siliceous refractory material, however, is quartzite or "ganister." Small lump or crushed quartz and quartzite are used in the bottoms of reverberatory furnaces and as acid-converter linings in copper and bessemer steel plants. Silica brick are the principal acid refractory products employed by metallurgists. Such brick usually are made from crushed ganister bonded with a small amount (1.5 to 2 pct) of lime. Quartzites ordinarily used in making silica brick contain about 98 pct silica and must be otherwise suitable for the purpose. In the United States the principal sources of raw materials are the Tuscarora (Medina) quartzite of Pennsylvania and the Baraboo quartzite of Devil's Lake region, Wisconsin. Other developed sources of raw material are Alabama, Ohio, Colorado, Utah, and California. The first silica brick were made from Dinas rock in Wales. Ganister deposits near Sheffield have also contributed extensively to the refractory requirements of Great Britain, and, indeed, largely influenced the location of the iron and steel industry. Typical analyses are given in Table 3.

TABLE 3—*Typical Analyses of Silica Brick*

Component	Composition, Pct	
	Pennsylvania Brick (Medina Quartzite)	Western Brick (Baraboo Quartzite)
Silica.....	95.67	95.50
Iron oxide.....	0.59	0.80
Alumina.....	0.92	0.98
Lime.....	2.24	2.30
Magnesia.....	0.27	0.22

The fusion point of silica brick is virtually the same as that of the more refractory fire-clay brick, but they have other characteristics that make them more suitable for many uses. They do not soften perceptibly at temperatures appreciably below the melting point. Their high thermal conductivity is also a factor contributing to their ability to retain their strength at high heats. Silica brick are used principally in the roofs of metallurgical furnaces, in coke ovens and gas retorts, and in other parts of structures where temperature changes are at a minimum, where volume stability and load-bearing properties are desired, and where there is not too much corrosion from basic slags. Silica brick show a thermal expansion of about 1.0 pct upon heating to 500°F, and this high thermal expansion is their main limitation because it causes the brick to spall or flake when suddenly heated or cooled.

Magnesite

Dead-burned magnesite is the principal basic refractory material and is employed wherever strongly basic slags are encountered in metallurgical furnaces at high temperature. It is obtained from two main sources. The larger part is prepared from the natural magnesium carbonate or magnesite rock found in the United States in Washington, in several countries of Europe, and elsewhere (see chapter on Magnesite).

The other important source is sea water. In the operations in New Jersey and California, magnesium hydrate is obtained from the sea water by treatment with dolomite or lime. Obtaining magnesite from sea water has several outstanding advantages: (1) all the raw materials are readily available in practically inexhaustible quantity, (2) the composition of the final product is under close control.

The dead-burned product is prepared by calcining the natural carbonate, such as that from Washington, or the hydrate from sea water at a temperature of 2730°F or higher to convert the magnesia to the crystalline form known as periclase, which in its pure state has a specific gravity of approximately 3.68. The calcined product varies in color from brown when the iron content is high to nearly white when the iron content is very low. Typical compositions of the most widely used types of dead-burned magnesites are shown in Table 4.

There are two principal uses for dead-burned magnesite: (1) for the construction and maintenance of rammed-in or sintered melting hearths of basic open-hearth and electric furnaces producing steel, (2) in the manufacture of magnesite or other basic refractory brick. The tonnages consumed in the two are about equal. Basic bricks are used in linings for certain parts of furnaces producing steel by the basic process; for furnaces smelting and refining copper and lead ores; for rotary kilns burning dolomite, portland cement and lime; and for furnaces in the chemical and paper industries treating sodium carbonate,

TABLE 4—*Analyses of Dead-burned Grain Magnesite*

Component	Composition, Pct		
	From Sea Water	Austrian	Washington
Ignition loss.....	0.49	0.10	0.03
Silica.....	5.64	4.50	6.90
Iron oxide.....	0.43	3.77	4.40
Alumina.....	0.17	1.61	2.01
Lime.....	1.41	2.64	5.28
Magnesia.....	91.86	87.38	81.38

sodium sulphate and other strongly basic oxides. Two general types of basic brick are available, the burned and the unburned. The manufacturing process by which these two types are produced is shown in the flowsheet of Fig 4.

Dolomite

Dolomite, a natural combination of magnesium and calcium carbonates, is much cheaper than magnesite and is used to some extent for furnace bottoms and widely for patching. The natural carbonates are calcined in rotary kilns after the manner of calcining magnesite. Other materials may be added to increase the content of iron oxide or other elements. The lime content is a disadvantage because it promotes slaking. Repeated attempts have been made to manufacture suitable dolomite brick, but today dolomite finds its principal use in dead-burned grain form or in the raw state. Dolomite is employed in sea-water processes producing magnesium hydrate. Mixed with magnesite or brucite, it is used for some refractory compositions.

Lime itself has been employed only to a limited extent as a refractory; it has a high melting point but absorbs moisture and certain gases too readily. A typical analysis of prepared dolomite is: SiO_2 , 1.80 pct; Al_2O_3 , 1.10; Fe_2O_3 , 5.87; CaO , 54.60; MgO , 36.40; ignition loss, 0.22.

Chrome Ore

Pure chromite is a mineral composed of 32 pct FeO and 68 pct Cr_2O_3 . However, in chrome ore, the commercial refractory material, these oxides are replaced in part by magnesia and alumina and the composition ranges from 30 to 48 pct Cr_2O_3 , 12 to 30 pct Al_2O_3 , 12 to 15 pct FeO , and about 17 pct MgO , along with some impurities, mainly SiO_2 . Chrome ore in lump or crushed form is used in maintaining certain parts of some metallurgical furnaces. The bulk of the chrome ore used in refractories, however, is made into chrome brick, or chrome-magnesite brick, the latter consisting of approximately 75 pct chrome ore and 25 pct magnesite. Chrome brick normally cost less than mag-

nesite brick and in some applications resist attack by basic oxide to an extent closely approaching that of magnesite brick. Accordingly, chrome brick, particularly the chrome-magnesite compositions, have found extensive use in metallurgical furnaces, particularly the basic open-hearth steel furnace. Chrome-magnesite brick are available in both burned and unburned types. The manufacturing processes are shown in Fig 4. Specific applications of the various types are described under Chrome Brick.

Spinel

Spinel is a compound of alumina with other metallic oxides in the form of aluminates, the type mineral being the magnesium aluminate ($\text{MgO} \cdot \text{Al}_2\text{O}_3$) containing 28 pct magnesia and 72 pct alumina. The melting point of the pure mineral is given as 2135°C . In addition to high melting point, all spinels are characterized by high specific gravity, high refractive index, extreme hardness and lack of cleavage. The natural mineral is widely distributed but rarely found in deposits of sufficient purity to make it economical to concentrate. Small seams occur in New England and New York but the largest deposit is said to be in India. Spinel produced synthetically in an electric furnace from oxides of magnesium and aluminum has not been used extensively because of its high cost. Spinel brick also have been made by mixing equal parts of magnesite and white bauxite, calcining at 1300°C or above, grading the product and forming into bricks by using a small amount of ball-clay binder, the final product corresponding to the formula of true spinel.

As a refractory, spinel has many valuable properties not possessed by either of its constituents (MgO or Al_2O_3). It is used also in refractory cement, as an abrasive and when well crystallized, as a gem stone.

Sillimanite and Mullite Group

The sillimanite group includes sillimanite, kyanite, and andalusite. These are identical from the standpoint of chemical composition and all are represented by the formula $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$, but they differ considerably in specific gravity and crystalline characteristics. When heated to moderate temperature, all of these minerals decompose and form mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) and free silica. Mullite, being relatively stable, is a highly desirable constituent in alumina-silica refractories. It is a mineral of rare natural occurrence and is generally formed by the decomposition of the sillimanite minerals or by heating mixtures of alumina and silica. Other minerals that give mullite when heated and that are of commercial interest in this respect are dumortierite and topaz.

Although all minerals of the sillimanite group are fairly common in nature, commercial deposits are rather rare. Sillimanite is found in massive form and in commercial quantities in Australia and in the states of

Rewa and Assam in India. Massive sillimanite has been found in Africa but it is too impure to be of value in refractories. Large deposits of sillimanite-bearing schist have been found in the states of South Carolina and Georgia.

The only known commercial deposit of andalusite occurs in the White Mountains near Bishop, California. This deposit yielded several thousands of tons of massive ore before it was abandoned in 1945. Andalusite schists are found in various localities but the mineral is usually heavily charged with iron and hence worthless.

Kyanite occurs much more widely in deposits of commercial size than do other minerals of the group, both massive and as small crystals in schists. Massive kyanite has been mined at the rate of 10,000 to 40,000 tons per year for more than 20 years in the state of Kharasawan, India. Material from this source is noteworthy in that it contains from 5 to 15 pct of corundum, is finely crystalline and does not expand greatly or "shatter" on being inverted to mullite.

Massive kyanite also occurs in large quantities in Kenya, Africa. Shipments from this source are now being made at the rate of 10,000 to 15,000 tons per year. The material is relatively pure but is coarsely crystalline and expands, and may shatter badly on inverting to mullite.

There are commercial deposits of massive kyanite in Australia but the ore seems to be too impure for general use.

Kyanite-bearing schists are widely distributed throughout the world. In the United States these schists have been worked commercially in North Carolina, South Carolina, Georgia, Virginia and California. The operations in Virginia and South Carolina are still active, producing recently about 15,000 tons yearly.

Products made essentially from kyanite include glasshouse refractories, ceramic-kiln furniture, electric-furnace linings, spark plugs, electrical porcelain, and chemical porcelain.

Zirconia

Zirconia is one of the most refractory substances known and is relatively inert to molten silicate slags and other corrosive agents. Zirconia crucibles were manufactured in Germany. Zirconia or zircon brick are also available. Although brittle in the unburned state, and rather costly, zirconia refractories are highly useful for certain special melting operations because of their high strength, hardness, freedom from spalling, and resistance to chemical and physical wear, mainly in precious-metal refining and in electric furnaces where exceptionally high temperatures are encountered. Zircon, the silicate, is likewise refractory and very resistant to thermal shock, but does not withstand the action of basic slags or iron oxide very well. Zircon refractories have been found useful in side walls of furnaces melting and refining aluminum scrap

and in furnaces producing some special glasses. Zircon cement is used as a protective coating on other refractories.

Brazil has been the principal source of world supply of zirconia ores (zirkite, baddeleyite, and others) but zircon is produced in increasing quantities also in British India, Australia, Florida, and elsewhere, frequently as a by-product of mining ilmenite-bearing and/or rutile-bearing beach sands.

Carbon and Graphite

Carbon, in the ordinary sense, is infusible. However, all varieties of carbon volatilize at very high temperatures and ordinary pressures without melting. Available forms for refractory materials are charcoal, coke and graphite. Brick made from ground coke, bonded with 20 pct tar, dried and baked, are available, and other kinds of carbon brick have been made from time to time. Bonded amorphous carbon, pure manufactured (electric-furnace) graphite, and bonded natural graphite are all on the market in various forms. Carbon brick are used extensively for lining the hearth and bosh sections of blast furnaces producing pig iron. Carbon refractories recently have found some application in Cottrell precipitators, for making acid, and for furnace linings and slag floors in high-pressure boiler furnaces where pulverized coal is used. Electric-furnace graphite is unique among refractories because of its purity, low linear expansion and nonfusibility; it retains its shape, size, structure, and physical properties under conditions of extremely high temperature. In short, carbon would be the ideal refractory if it were not for the fact that it is consumed rapidly at temperatures above bright red heat in an oxidizing atmosphere or when in contact with fused oxides of many metals. Graphite crucibles still find extensive application in the melting of metals. They contain 25 to 75 pct of graphite bonded with fire clay.

Silicon Carbide and Fused Alumina

Silicon carbide, SiC , a crystalline product of the electric resistance furnace, is generally considered to be formed at approximately 3350°F or higher and to dissociate at approximately 4550°F . Softening or fusion does not occur below the dissociation temperature. Excellent resistance to abrasion accrues from its hardness, which is approximately 9.6 on the Mohs scale. It is inert to most acids, either liquid or gaseous, but may react with alkalis, molten iron or steel, some metallic oxides, and basic slags at moderate or high temperatures.

Silicon carbide refractories have come to be widely used and many types of bonds are employed to produce refractories having a wide range of properties and high resistance to the factors adversely affecting service life. Being especially resistant to the destructive action of coal-ash

clinker, acid slags, and abrasion, they find considerable usage in boilers, water-gas generators, gas producers, and in heat-treating, annealing, forging, nonferrous melting furnaces, and similar processes. Thermal conductivity is high, ranging from 100 to 108 Btu per square foot per inch thickness per degree F per hour in the temperature range of 1200° to 2800°F. Because of this property, silicon carbide refractories are used extensively in coking and calcining retorts, zinc retorts, porcelain enameling furnaces, tunnel and periodic kilns, glass lehrs, roasting furnaces, recuperators, regenerators, cracking and "fixing" checkers.

Fused alumina is produced in electric-arc furnaces by heating bauxite ore with purifying agents to the temperature of fusion, which is approximately 3650°F.

Many special tile, blocks, and brick shapes are fabricated from crushed and graded fused alumina for batch and continuous porcelain enameling furnaces, tunnel-kiln muffles, and other uses where great refractoriness, high load-carrying capacity, medium thermal conductivity, and other properties render it particularly applicable.

Refractory Ware for Extra High Duty

For certain special small-scale work, demand exists for ware to withstand temperatures substantially higher than usually are encountered in commercial work, chiefly in the form of crucibles and ignition boats:

Alumina (99 pct Al_2O_3) melts at 2040°C (3704°F), softens above 1900°C (3452°F), furnished: (1) porous in large sizes to resist temperature changes, or (2) porcelain-hard and translucent. At high temperatures more acid than neutral, not at all basic.

Magnesia (95 pct MgO) does not soften up to 2000°C (3632°F); is serviceable up to 2400°C (4352°F), porous, and highly resistant to changes in temperature. At high temperatures is faintly basic or neutral; does not form carbide but vaporizes in reducing atmosphere.

Magnesia (99 pct MgO) melts at 2800°C (5072°F). Is very dense and translucent, like porcelain.

Beryllia (99 pct BeO) melts at 2510°C (4550°F) and may be used above 2000°C (3632°F). Porcelainlike translucent body suitable for crucibles of neutral character, replacing alumina when higher temperatures preclude use of alumina.

Zirconia (96 pct ZrO_2) melts above 2600°C (4712°F) and may be used up to 2500°C (4532°F). Can be furnished in porous or denser form, according to size and shape of article. Sensitive to temperature changes but particularly resistant to chemical action of all kinds; does not vaporize appreciably in reducing or oxidizing atmosphere, but forms thin layer of carbide in contact with carbon at high temperatures.

Thoria (99 pct ThO_2) melts at 3050°C (5522°F) and may be used up to 2500°C (4532°F), or above. Chemical properties similar to those of zirconia but more basic.

Miscellaneous Refractories

Titanium oxide or rutile has been formed into brick by using lime as binder and is reported to have proved satisfactory as an acid refractory.

Bone ash, made by calcining bones, formerly was used extensively for cupels in commercial silver refining as well as in assaying, but now is largely replaced by other materials. Fused-silica ware and porcelain are also classed as refractories, and certain varieties of glass (e.g., combustion tubing and special oven ware) fall into the same category. Ceria and mixtures of the oxides of the rare earths are refractories but are far too expensive to be used in commercial equipment.

It is not customary to consider the metals as refractories, but they are so used to a considerable extent. Ordinary cast iron, mild steel, and wrought iron are widely employed in services in which they are exposed to moderately high heats, and the new stainless and heat-resisting alloys recently developed will withstand higher temperatures. Nickel and copper find many high-temperature uses and, in a much smaller way, platinum and certain allied metals have highly important applications in the broad realm of refractory uses.

Various naturally occurring minerals and rock formations have been employed as furnace linings. Mention has been made of mica schist, sandstone and quartzite, which probably are most important, but soapstone has found applications because it not only is refractory but also is readily sawed and otherwise formed to the desired size and shape; it has been used principally in alkali-recovery furnaces in paper mills. Talc has similar advantages and certain varieties that exhibit no distortion when fired are employed in sundry small articles, including the so-called "lava" tips for gas burners and gas-mantle rings. Pyrophyllite likewise is receiving serious consideration, both in block form and in the batch, as a constituent of synthetic refractories. Olivine or dunite has been employed experimentally on a large scale to replace chromite in steel furnaces; almost unlimited supplies of this magnesium silicate and of pyrophyllite (aluminum silicate) practically free from iron are available at low cost in North Carolina. The use of olivine mixed with magnesite and made into brick having a composition approaching that of forsterite has been extensively tried but has found only minor applications in recent years.

Various mixtures of refractory materials may also be mentioned. The most important are the high-alumina fire-clay mixtures, already

discussed. Asbestos-clay brick are mentioned in certain textbooks as used for partitions but inasmuch as chrysotile asbestos is altered and embrittled at temperatures below the firing temperature of most firebrick, such mixtures are of doubtful value. Insulating firebrick of light weight and highly porous character are commonly manufactured from clays mixed with an organic material. During the firing treatment, the organic material-sawdust, cork, etc.—is burned out, leaving pores. The amount and size of pores is adjusted by the amount, size and shape of the organic material. More or less refractory mixtures containing diatomite, vermiculite, perlite, or pumice are also used for moderately high-temperature insulating purposes.

The American Society for Testing Materials classifies insulating firebrick into group identifications as shown in Table 5.

TABLE 5—*ASTM Classification of Insulating Firebrick*

IDENTIFICATION	PERMANENT LINEAR CHANGE	BULK DENSITY,
	NOT MORE THAN 2 PCT WHEN TESTED AT:	LB PER CU FT Not greater than:
Group 16	1550°F (845°C)	34
20	1950°F (1065°C)	40
23	2250°F (1230°C)	48
26	2550°F (1400°C)	52
28	2750°F (1510°C)	60

Insulating firebricks are used in furnaces to reduce heat capacity and conserve heat fuel.

Grouping According to Raw Materials Required

According to the raw materials required, the refractory industry is roughly separable into the manufacture of fire-clay and silica refractories as a major group and the production of other refractories as a minor group. In general, the former group comprises plants producing relatively cheap tonnage products while the latter comprises the highly diversified industry that caters to the demand for high-duty refractories to meet more exacting requirements, which therefore cost more. Compared with the ordinary run of heavy clay products, however, even the cheapest refractory material is relatively high in price; and ordinary firebrick grade more or less insensibly into high-duty firebrick as better and more expensive materials or mixtures of materials are employed. There is an economic point in attempting to draw a distinction, however, to the extent that a cheap raw material like ordinary fire clay must find its market fairly close to the point of origin whereas magnesite and chrome are carried halfway around the world from the mines to the brickworks.

METHODS OF MANUFACTURE

Fire-clay Brick

The three general methods used in manufacturing fire-clay brick are hand molding, stiff-mud repressing, and dry pressing. Hand molding is used mainly in the manufacture of shapes that are very large or have very irregular contour. The bulk of fire-clay brick is manufactured by the two other processes and the choice between them depends upon the nature of the raw materials and the properties desired in the finished brick. The various manufacturing steps involved in the three processes are shown in Fig 2.

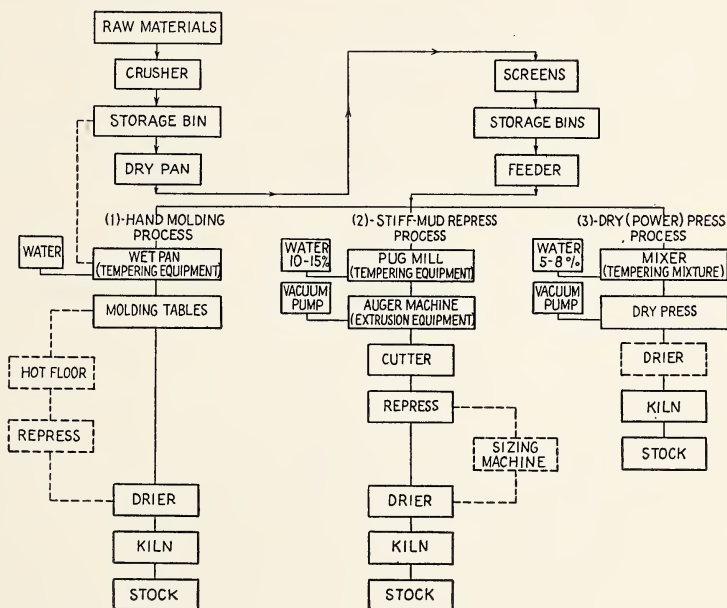


FIG 2—THREE METHODS OF MANUFACTURING FIRE-CLAY BRICK.

The three principal raw materials are flint clay, bond clay, and grog or calcine. The flint clay makes up the bulk of the brick. It is very hard and refractory. Some flint clays can be processed without the addition of bond clay; others cannot. Bond clay, a plastic material somewhat less refractory than flint clay, is used mainly to impart bond or strength to the brick to facilitate processing and handling in the green state. Where flint clays are extremely low in plasticity, the use of bond clay also helps in the burning operation. Grog or calcine is used mainly to control shrinkage in burning. Grog may consist of brick that have been ground to the required screen analysis or may be a clay that is calcined in the lump form as it comes from the mines and then crushed or ground.

As shown in the flowsheet (Fig 2), the general method of preparing the clays for any of the three processes of manufacture is about the same up to the molding operation. Occasionally, where the clays being ground and prepared are very uniform in hardness, the mix for hand molding may be ground directly in the wet pan or tempering machine. Some hand-molded shapes are allowed to dry somewhat and are repressed to improve workmanship; others are merely touched up at the corners and set directly from the molding tables into the drier.

In the stiff-mud repress process, some manufacturers put the green brick through a sizing machine to improve the workmanship. In the manufacture of dry-press brick, it is the general practice to set the brick right from the press into the kiln, although sometimes a drier is used. Dry-pressed brick are somewhat cheaper to manufacture than stiff mud. The brick are formed under relatively high pressures, ranging from 1000 to 5000 psi, and have virtually no drying shrinkage.

Fire-clay brick manufactured by the stiff-mud repress method are usually harder, tougher, and denser than dry-press brick. They are used where resistance to erosion by molten slag or resistance to abrasion are the outstanding requirements.

Brick made by any of the three processes are fired both in tunnel and periodic kilns. Where large, steady production is available, the tunnel kilns are economical. Fire-clay brick are burned at temperatures anywhere from 2200° to 2450°F, again depending upon the nature of the raw materials and the properties desired in the finished brick.

Superduty and high-fired superduty fire-clay brick are manufactured usually by the dry-press method. Shapes that cannot be adequately formed because of size or contour are frequently rammed in steel molds with air hammers. Selected flint clay is used ordinarily with a minimum amount of bonding clay. Superduty fire-clay brick are burned at a temperature of approximately 2450°F. High-fired superduty fire-clay brick are commonly burned at a temperature of 2600°F; higher for special jobs. These brick, because of shrinkage in firing, require special settings in kilns to ensure sound brick and good workmanship.

Silica Brick

Three general processes are used for the manufacture of silica brick—hand molding, machine molding, and dry pressing. The various steps involved in each method of manufacture are shown in Fig 3.

Ganister, the essential raw material, is a massive crystalline quartzite. It is broken down in crushers of the jaw or gyratory type and in the hand-molding and machine-molding processes is ground to the desired screen size in a wet pan, where approximately 2 pct of lime is added. In hand molding, the shapes are prepared by pounding the mix into molds with heavy mauls. In machine molding, the mix from

the wet pan is sent to an overhead bin and dropped about 15 ft into the molds on a molding table below. In the dry-press process, which is comparatively new, the crushed ganister is ground dry in a dry pan or other grinding mill and screened to the desired screen analysis. Pressing is done on a machine similar to that used for the manufacture of fire-clay brick.

Silica brick are very difficult to fire satisfactorily and must be handled carefully because of some of the sudden expansion changes during burning. Firing usually is done at about 2700°F in periodic kilns.

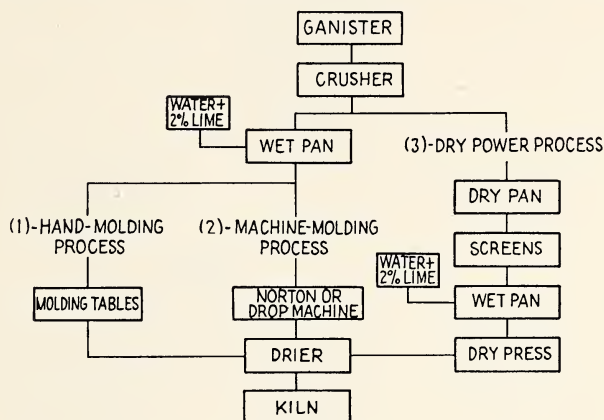


FIG 3—THREE METHODS OF MANUFACTURING SILICA BRICK.

One tunnel (continuous) kiln, however, is now in operation in this country. Machine molding is used mainly for small shapes of regular contour. Hand molding is used for the larger shapes and the bulk of the silica-brick production is made by this method of manufacture. The dry press can make larger shapes than the machine and also improves workmanship. The properties of the finished brick will vary somewhat, according to the nature of the raw material.

Magnesite Brick

Two general types of magnesite brick are available, burned and unburned. The latter constitutes the bulk of the production. The flowsheet in Fig 4 shows in general the steps involved in the manufacture of burned brick and the two types of unburned brick.

The principal raw material is dead-burned grain magnesite. This is ground in a dry pan and screened carefully over vibrating screens. The screened particles are charged into tempering pans, where water and bonding agents are thoroughly worked into the grains. The molding of the brick may be done on hydraulic presses or with conventional mechanical dry power presses similar to those used in the manufacture of dry-press fire-clay and dry-press silica brick. After form-

ing, the bricks are given the necessary curing and dry treatment. The unburned brick are ready for shipment while those to be burned are set in periodic or tunnel kilns. The firing process requires a great deal of care. In the periodic kilns or when the shapes are large, each brick is supported by a silica brick that has already been burned and is of no value. The firing is carried to approximately 2700°F. Burned magnesite brick are very sensitive to thermal shock and their use is limited to conditions in which there is a minimum of thermal shock. Typical ap-

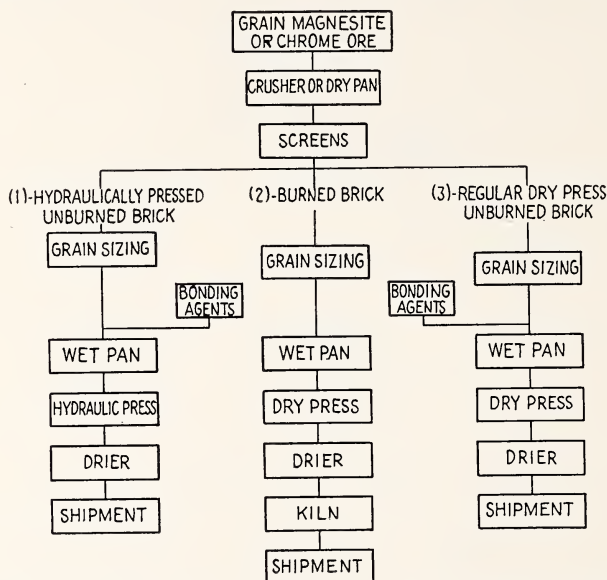


FIG 4—MANUFACTURING METHOD FOR BURNED MAGNESITE AND CHROME BRICK AND TWO METHODS FOR UNBURNED BRICK.

plications are in basic open-hearth furnaces under the grain-magnesite hearths, in copper-refining furnaces below the metal line, and in copper converters where protective coating of magnesite is maintained.

The unburned brick, particularly those made with careful grain sizing and at high molding pressure, are characterized by high density and low porosity. Their strength is satisfactory at all temperatures. Compared with burned magnesite brick, unburned brick cost less and are more resistant to spalling. These considerations combine to make unburned brick more generally useful. Typical uses of the unburned brick are in the exposed walls of the basic open-hearth furnace, hot-metal mixers, roofs and walls of copper-smelting and copper-refining furnaces, copper converters, hot zones of rotary kilns burning dolomite, portland cement and lime, checkers of glass-melting furnaces.

Another feature of the chemically bonded brick is that during manufacture it can be sheathed with thin sheet steel. When so made and put

in service, the steel in the joints unites the individual bricks, further increases resistance to spalling, and results in longer life. Such metal-clad bricks are being found most economical in open-hearth furnace front walls and end walls where at one time only chrome-magnesite bricks were used.

Chrome and Chrome-magnesite Brick

There are two general classes of chrome brick: (1) a brick consisting entirely of chrome ore, (2) chrome-magnesite brick.

The chrome brick is burned and the manufacturing process is similar to that for burned magnesite brick. Burned chrome brick, like burned magnesite brick, are very sensitive to thermal shock and their use is limited to places in which there is little thermal shock. A typical use is in the hearths of some basic open-hearth steel furnaces below the metal line and under the magnesite grain hearth.

Chrome-magnesite brick contain approximately 75 pct chrome ore and 25 pct magnesite. They are available burned or unburned. Most of the latter are made by hydraulic pressing, the remainder by conventional dry pressing. The manufacturing processes are generally similar to those used for unburned magnesite. Chrome-magnesite brick, particularly those that are hydraulically pressed and chemically bonded, are more resistant to thermal shock than burned chrome brick and cost less than their equivalent types in magnesite. Consequently, they are used extensively in front walls and end walls of basic open-hearth steel furnaces, to some extent in copper-refining furnaces and copper converters, and in walls and bottoms of paper-plant recovery furnaces.

High-alumina Brick

Highly aluminous refractories are manufactured in much the same general way as fire-clay brick, except that burley and diasporic clays, obtained mainly in the state of Missouri, and imported bauxite are substituted for flint clay and the formed brick are burned at temperatures comparable to those used for the superduty fire-clay brick. For special purposes, other highly aluminous refractories are made by using kyanite or sillimanite instead of burley or diasporic.

Miscellaneous Refractories

Zircon or Zirconia Brick usually are molded in a dry press from crushed ore, fines of the same material proving the best binding agent.

Silicon Carbide Refractories are made in many varieties employing properly sized grain and many different types of bonds. As new applications have arisen and additional problems have had to be solved, silicon carbide refractories have been progressively modified through the years to produce types to withstand the chemical and physical condi-

TABLE 6—*Production of Firebrick and Allied Fire-clay Products, by Kinds and States, 1929 and 1939^a*

Kind and State	1929			1939		
	Num- ber of Plants	Quan- tity	Value, Thou- sands of Dollars	Num- ber of Plants	Quan- tity	Value, Thou- sands of Dollars
		Thou- sands			Thou- sands	
Brick, block of firebox tile (9-in. equiv.): total.....	198	938,218	\$36,169	160	507,324	\$26,169
Alabama.....	2	<i>b</i>	<i>b</i>	3	14,959	632
California.....	16	26,714	1,330	18	16,085	931
Colorado.....	6	16,083	595	5	8,071	344
Illinois.....	3	25,216	796	5	6,954	254
Indiana.....	4	5,867	136	<i>b</i>	<i>b</i>	<i>b</i>
Kentucky.....	11	101,818	4,474	10	51,501	2,655
Mississippi.....				3	220	3
Missouri.....	13	153,505	5,968	11	99,948	5,208
New Jersey.....	10	17,450	928	6	10,139	625
Ohio.....	25	152,175	3,966	27	96,579	3,368
Pennsylvania.....	59	352,421	14,897	39	155,780	8,550
Texas.....	7	6,799	223	6	6,513	172
Washington.....	5	6,715	254	<i>b</i>	<i>b</i>	<i>b</i>
Other states.....	37	73,455	2,601	27	40,575	3,357
High-alumina brick: total....	17	23,911	2,115	28	16,714	1,512
Missouri.....	6	6,716	542	9	9,425	885
Ohio.....	4	8,175	469	4	2,451	111
Pennsylvania.....	1	<i>b</i>	<i>b</i>	5	1,323	83
Other states.....	6	9,020	1,104	10	3,515	433
		Tons			Tons	
Special shapes: total.....	53	182,280	4,092	60	151,511	3,833
California.....	7	6,961	196	11	8,772	253
Missouri.....	7	76,418	1,532	<i>b</i>	<i>b</i>	<i>b</i>
New Jersey.....	4	5,551	263	<i>b</i>	<i>b</i>	<i>b</i>
Ohio.....	6	12,333	298	7	21,312	461
Pennsylvania.....	15	50,416	1,085	13	32,117	1,033
Other states.....	14	30,601	719	29	89,310	2,085
Plastic firebrick (ramming): total.....	<i>c</i>	<i>c</i>	<i>c</i>	41	43,679	1,120
California.....	<i>c</i>	<i>c</i>	<i>c</i>	5	961	32
Ohio.....	<i>c</i>	<i>c</i>	<i>c</i>	6	8,389	186
Pennsylvania.....	<i>c</i>	<i>c</i>	<i>c</i>	8	5,283	83
Other states.....	<i>c</i>	<i>c</i>	<i>c</i>	22	29,046	819
Total ^d	<i>c</i>	<i>c</i>	<i>c</i>	11	59,783	1,575

TABLE 6—(Continued)

Kind and State	1929			1939		
	Num- ber of Plants	Quan- tity, Tons	Value, Thou- sands of Dollars	Num- ber of Plants	Quan- tity, Tons	Value, Thou- sands of Dollars
Glasshouse tank blocks, pots, etc.: total.....	13	35,912	2,276	15	26,956	2,339
Indiana.....	2	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
Ohio.....	2	<i>b</i>	<i>a</i>	3	7,556	432
Pennsylvania.....	5	8,125	545	6	<i>b</i>	<i>b</i>
Other states.....	4	<i>b</i>	<i>b</i>	12	19,400	1,907
Refractory cement (clay): total.....	48	57,532	1,693	60	47,178	2,491
California.....	6	5,306	88	6	1,507	93
Illinois.....	2	<i>b</i>	<i>b</i>	4	1,548	34
Missouri.....	7	<i>c</i>	<i>c</i>	8	17,844	1,032
New Jersey.....	4	<i>a</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
New York.....	6	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
Ohio.....	4	2,292	84	8	3,346	154
Pennsylvania.....	12	<i>b</i>	<i>b</i>	13	9,168	379
Other states.....	7	<i>b</i>	<i>b</i>	21	13,416	801
Other fire-clay products and fire-clay dust: total.....	71	<i>b</i>	3,503	33	<i>b</i>	2,458
Colorado.....	1	<i>b</i>	<i>b</i>	4	<i>b</i>	64
Illinois.....	8	<i>b</i>	950	<i>b</i>	<i>b</i>	<i>b</i>
Ohio.....	18	<i>b</i>	1,467	8	<i>b</i>	871
Pennsylvania.....	6	<i>b</i>	<i>b</i>	7	<i>b</i>	1,057
Other states.....	38	<i>b</i>	1,086	14	<i>b</i>	465

^a Compiled from a report of the U. S. Bureau of the Census.^b Figures included under "other states."^c Data not available.^d Missouri, Ohio, Pennsylvania, West Virginia, Colorado and Illinois were producing states in 1939.

tions being imposed by many newly developed types of equipment and processes requiring the application of heat.

Fused Cast Refractories, formerly available only in mullite, are now produced in various compositions of mullite and zirconia, also high-alumina compositions containing 80 to 95 pct alumina. Originally employed solely in the glass industry, they are now used for other applications where high resistance to slags, fluxes, and abrasion is required. Although most fused cast refractories are susceptible to thermal shock, one high-alumina variety is being employed extensively in glass-tank superstructures.

HISTORY OF THE INDUSTRY

Ancient Egyptian and Assyrian records indicate that the manufacture of clay brick was one of the earliest established industries, and the use of refractories of a sort has been a necessary accompaniment of all high-temperature processes since the beginning of man's use of fire. However, the early metallurgists built their own furnaces from available materials and the manufacture of refractories did not emerge as a separate industry of importance until comparatively recently. The zinc-smelting industry still produces some of its own refractories, notably retorts and condensers.

TABLE 7—*Production of Fire Clay in the United States, 1900–1946^a*

Five-year Average	Short Tons	Value	Year	Short Tons	Value
1900–1904	990,944	\$1,226,800	1940	2,765,247	\$ 7,046,746
1905–1909	1,330,016	1,806,102	1941	4,167,567	10,455,909
1910–1914	1,618,207	2,274,754	1942	4,839,332	11,381,506
1915–1919	2,007,326	4,397,451	1943	4,701,144	11,169,922
1920–1924	1,995,774	5,716,974	1943 ^b	7,798,223	17,218,446
1925–1929	2,810,001	7,747,918	1944 ^b	6,344,383	14,167,118
1930–1934	1,433,784	3,748,668	1945 ^b	6,090,411	15,587,034
1935–1939	2,175,309	5,858,058	1946 ^b	7,907,774	20,827,220

^a Sales by producers (except as noted in 1944 and later years) as reported in Minerals Resources of the United States and the Minerals Yearbook (annual volumes); does not include kaolin, ball clay, bentonite, and certain other clays used in manufacture of fire-brick, fire-clay mortar, or other refractory uses.

^b Includes fire-clay used in producers' plants as well as sales (captive tonnage).

In colonial days the iron furnaces and primitive forges were constructed of stone and firebrick did not come into general use, in the United States at least, until well along in the nineteenth century. Sandstone was used even for the walls of kilns burning refractories.¹⁴ Norton (p. 12 of ref. 8) infers that the first clay refractories used in this country were glass pots and German pot clays were imported and probably used more or less extensively in the various glass plants built before the American Revolution, many of which were operated by Germans. The manufacture of glass pots as an industry separate from the glass plants was begun in Pittsburgh¹⁰ in 1860 by Thomas Coffin. The Pittsburgh Clay Pot Co. was organized in 1879 and subsequently many other concerns opened for business in Pennsylvania and Ohio.

The production of firebrick in the United States probably dates back to 1812, by a factory said to have existed in New Jersey, but firebrick may have been manufactured even earlier in Boston or Baltimore. In 1837 the Mt. Savage fire clay was discovered but firebrick were

TABLE 8—Sales of Raw Clay for Specified Refractory Purposes^a

SHORT TONS, COMPARED WITH TRADE INDEXES

Use	1925-29 ^b	1930-34 ^b	1935-39 ^b	1940	1941	1942	1943	1944	1945	1946
Firebrick.....	1,001,089	639,772	1,236,728	1,650,802	2,566,373	3,265,222	3,070,364	3,791,083	3,495,982	3,475,090
High-alumina brick.....	3,450	6,784	11,590	16,646	105,077	77,478	65,921	78,981	67,654	89,774
Fire-clay mortar.....	428,910	231,001	215,730	208,398	286,231	312,597	337,049	213,329	190,357	224,303
Clay crucibles.....	2,626	1,600	634	1,761	4,736	2,099	18,488	4,420	2,646	5,737
Glass refractories.....	38,546	23,867	4,758	975	45,278	22,646	17,627	16,685	10,627	19,327
Zinc retorts.....	59,591	13,052	12,407	27,495	40,966	45,851	58,076	57,358	46,980	56,898
Foundries, steelworks.....	532,125	250,553	492,162	684,271	936,596	995,841	1,025,827	1,121,189	915,569	867,630
Other refractories.....	2,529	573	27							528,774
	2,068,966	1,167,292	1,974,030	2,590,348	3,985,247	4,721,734	4,593,352	5,283,025	4,729,815	5,267,533

Index Numbers (1925-1929 = 100)

Raw-clay sales.....	100	56	95	125	194	228	222	255	228	255
Fire clay.....	100	51	77	98	148	172	^c	^c	^c	^c
Iron and steel production.	100	52	86	126	159	170	178	177	150	128
Industrial activity.....	100	75	102	127	165	203	244	240	207	173

^a As reported by producers to the Bureau of Mines.^b Yearly average.^c Figures not comparable with figures published in table on uses in Minerals Yearbook 1943 because they include captive tonnage of clay burned into clay products at mine or pit.

TABLE 9—*Production of Specified Refractory Products^a*

Kind	1925-1929, Average		1932		1943	
	Quan- tity	Value, Thou- sands of Dollars	Quan- tity	Value, Thou- sands of Dollars	Quan- tity	Value, Thou- sands of Dollars
Clay products, thousands: brick, block, or firebox tile (9-in. equiv.).....	931,481	\$36,947	217,412	\$7,611	794,170	\$50,514
High-alumina brick ^b	12,637	1,211	4,864	464	27,967	4,056
Special fire-clay shapes, tons..	115,870 ^c	2,756 ^c	85,998	1,849	312,885	16,763 ^d
Glasshouse tank blocks, pots, tons.....	37,534 ^e	2,193 ^e	15,869	908	29,787	2,741
Refractory cement (clay), tons..	46,322 ^e	1,299 ^e	21,766	866	146,771	8,199
Clay sold raw or prepared, tons..	518,351	2,738	134,815	686	780,842	3,496
Other clay products, tons.....	<i>g</i>	5,004 ^f	<i>g</i>	694	630,986	14,847
Silica brick, thousands.....	256,818	13,001	40,111	1,762	320,329	21,821
Magnesite and chrome brick, thousands.....	14,864	4,433	3,167	845	51,146	17,638
Graphite crucibles, ^h tons.....	<i>i</i>	2,336	2,127	639	<i>g</i>	<i>g</i>
Silicon-carbide refractories.....	<i>i</i>	<i>i</i>	<i>i</i>	<i>i</i>	4,272	5,446
Refractory cement (nonclay) tons.....	64,255 ^e	1,337 ^e	16,693	444		
Others (including fused alumina, kyanite, forsterite, zircon, etc.), tons.....	<i>g</i>	5,257	<i>g</i>	2,414	8,908	9,377

^a Compiled from U. S. Bureau of the Census Reports.^b Over 40 pct Al_2O_3 in 1925-1929 and in 1932; over 50 pct Al_2O_3 in 1943.^c Four-year average.^d Includes insulating refractories (32,813 M); sleeves, nozzles, etc. (49,579 M), and ladle and hot tops (230,493 M).^e Three-year average.^f Includes some duplication.^g Data not available.^h Average 1925, 1927 and 1929ⁱ Silicon carbide included with "others" prior to 1943.

being made in Baltimore before that date and Ries and Leighton¹⁰ state that records show a shipment of firebrick from Florida to New Orleans in 1827. The Ohio industry was established at East Liverpool in 1841 but by that time the New Jersey and Pennsylvania industries had been in steady operation for some years. Several firebrick companies were in business in Missouri in 1855 and shortly after the Civil War (in 1866) firebrick were being made at Golden, Colorado, which remained the western outpost of the industry for several decades. The California and Washington plants are of relatively recent establishment.

According to Norton (pp. 19–20 of ref. 8), probably the first silica brick made in the United States were manufactured at Akron, Ohio, in 1866; later they were made at Niles, Ohio, in 1872, and at Perth Amboy, New Jersey, in 1875. Although the modern lime-bonded silica brick was developed even later, U. S. Patent 20433, issued to Thomas James in 1858, indicates actual experience in the production of these refractories, and the earliest production of lime-bonded brick preceded this by a few years, in England. Steel manufacturers began to use chrome brick about 1896. Magnesite was not used successfully in the United States until 1888 although it was in regular use in Europe about 1880. High-alumina refractories are of recent development and Missouri diaspore was not recognized as a source of material for especially good refractories until 1917. Sillimanite, kyanite and mullite refractories were all introduced after the close of World War I.

WORLD PRODUCTION

The production of firebrick and other refractories has been well established in Germany, Belgium, Great Britain, France, and Italy, as well as in the United States, and various other industrial countries have refractory-producing industries of at least local importance. There is a natural tendency to develop local industries wherever suitable raw materials are available and a market exists. Magnesite brick, for example, are normally made in substantial quantities in Austria and Czechoslovakia for home consumption and export. In at least two countries—Belgium and Poland—the existence of suitable clay deposits, accompanied by fuel supplies, encouraged the establishment of important zinc-smelting industries that otherwise might have been established elsewhere. Even in the British Isles, there is reason to believe that the many occurrences of good refractory materials have been a favorable factor in the development of local ironworks and steelworks and other industries that utilize refractories in high-temperature processes. The growth of a flourishing refractories-manufacturing industry in Germany was due in part to the possession of a few beds of superior clays but perhaps to an even greater extent to thorough development and organization.

DOMESTIC INDUSTRY

Production

Complete statistics showing the total output of refractories in the United States are not available and any aggregate figures that may be compiled are subject to discussion as to the character and variety of items included. Chemical or electrical porcelain and chemical stone ware, for example, may be classed as refractories, and there are numerous articles, such as saggars or zinc retorts, that ordinarily are made

TABLE 10—*Production of Refractory Brick in the United States, 1911–1945^a*

Year	Clay Firebrick		High-alumina Brick (Over 40 Pct)		Silica Brick		Magnesite and Chrome Brick	
	Quantity, Thousands	Value, Thousands of Dollars	Quantity, Thousands	Value, Thousands of Dollars	Quantity, Thousands	Value, Thousands of Dollars	Quantity, Thousands	Value, Thousands of Dollars
1911–1914 ^c	753,317	\$14,699	<i>b</i>	<i>b</i>	108,800	\$ 3,053	<i>b</i>	<i>b</i>
1915–1919 ^c	1,098,031	34,481	<i>b</i>	<i>b</i>	247,586	11,165	<i>b</i>	<i>b</i>
1920–1924 ^c	932,475	39,381	<i>b</i>	<i>b</i>	200,969	10,154	<i>b</i>	<i>b</i>
1925–1929 ^c	931,336	37,735	15,766	\$1,211	256,818	13,001	14,864	
1930–1934 ^c	427,025	16,327	9,798	906	114,146	5,755	8,926	\$2,526
1935	481,679	19,496	13,220	1,071	149,621	8,180	12,112	3,425
1936	615,498	26,580	11,151	1,122	229,325	12,453	20,403	5,676
1937	700,947	32,806	27,459	2,134	220,110	12,802	22,758	6,727
1938	349,153	17,236	16,095	1,724	90,952	5,473	12,060	3,675
1939	507,324	25,169	16,714	1,512	175,376	9,086	24,987	7,478
1940	612,128	29,989	17,879	1,850	216,721	12,214	29,557	9,464
1941	782,182	43,457	19,059	2,864	310,680	19,962	45,140	15,049
1942	910,535	55,901	21,818	3,459	374,757	24,112	49,567	17,144
1943	794,170	50,514	27,967	4,056	320,329	21,821	51,146	17,638
1944	617,620	38,102	23,668	3,363	288,258	18,673	47,645	16,375
1945	600,905	38,584	16,292	2,523	270,830	18,476	47,026	16,093

Refractories	1941		1942		1943		1944	
	Quantity, Thousands	Value, Thousands of Dollars	Quantity, Thousands	Value, Thousands of Dollars	Quantity, Thousands	Value, Thousands of Dollars	Quantity, Thousands	Value, Thousands of Dollars
Fire-clay brick.....	721,201	\$38,878	832,789	\$49,419	720,622	\$44,042	547,501	\$32,134
Superduty brick.....	60,982	4,579	77,746	6,483	73,548	6,471	70,119	5,968
Insulating refractories.....	29,152	3,099	44,599	4,290	32,813	3,220	18,167	1,834

^a Compiled from reports of the U. S. Geological Survey and U. S. Bureau of the Census.^b Not separately reported.^c Yearly average.

by the consumer for his own use. Any statements as to the expansion of total domestic production, therefore, are subject to modification, owing to changes in the variety of items classed as refractories for which statistics are available. Moreover, the apparent expansion is to a small but appreciable extent due to increased coverage in statistical canvasses.

From available data, however, it appears that during the late 1920s the aggregate value of the products of the domestic refractories indus-

tries was of the order of \$90,000,000 to \$100,000,000, or, roughly, equal to the normal output of pottery products in the United States. In 1939, the output of refractories was valued at \$65,315,000 and in 1945 it had risen to \$136,561,000, of which \$67,775,000 represented clay products and \$68,786,000 nonclay refractories. The number of employees has been estimated at around 19,000. Plant capacity is vastly in excess of domestic needs, even in active years. Attention should be drawn, moreover, to the close correlation between the refractories in-

TABLE 11—*Number of Establishments Producing Specified Products in the United States, 1925-1945*

Products	1925	1929	1932	1934	1939	1940	1945
Clay products:							
Clay firebrick, etc.....	238	198	178	181	160	182	118 ^a
High-alumina brick.....	10	17	12	25	28	29	13
Special shapes.....		53	73	69	60	65	43
Glasshouse refractories..		13	16	16	15	20	
Cement.....	38	48	51	57	60	69	58
Nonclay products:							
Silica brick.....	28	26	25	28	27	27	25
Magnesite brick.....	7	4	3	4	5	6	4
Chrome brick.....	4	3	3	4	5	6	4
Cement.....	^b	18	24	23	10	10	23
Other ^c	16	20	29	25	35	32	17

^a Fire-clay brick and standard shapes only (excluding superduty); the total number of establishments producing clay refractories in 1945 was 213.

^b Nonclay cement included with clay cement in 1925.

^c Includes alumina and silicon-carbide refractories.

dustries and iron and steel production. Except for the changes in coverage of the canvass in 1943, shipments of fire clay as reported by the Bureau of Mines afford an excellent barometer of the state of the refractories industries, as may be seen in Table 8.

Geographical Distribution

Pennsylvania is by far the leading source of domestic refractory products, furnishing in recent years substantially more than one third of the clay firebrick and a majority of all the silica brick produced in the United States, as well as considerable numbers of the magnesite brick, chrome brick, and other special refractories. In numbers of establishments, Missouri, Ohio and Kentucky normally follow Pennsylvania in about the order named. The industry is represented in at least 33 states but the four leading states account for roughly 80 pct of the total quantity of firebrick and an even larger percentage of the total value of all refractory products. The reason for the concentra-

tion of the industry in a relatively small number of important centers is indicated in part by statistics of fire-clay production, which show that recently more than two thirds of the tonnage of this important raw material has been mined in the four states mentioned. Nearness to markets in the leading iron and steel districts and transportation facilities are other factors.

TABLE 12—Imports of Refractory Brick for Consumption in the United States, 1936-1946

Year	Fire-clay Brick		Silica Brick		Magnesite Brick		Chrome Brick
	Thou- sands	Value	Thousands	Value	Thou- sands	Value	
1936.....	781	\$34,283			0.87	\$143	
1937.....	712	37,601			^a	122	
1938.....	523	40,995			1.08		N
1939.....	458	28,966				3,570	O
1940.....	373	18,815					I
1941.....	728	37,408					M
1942.....	791	58,320					P
1943.....	760	62,144					O
1944.....	734	57,191			8.6	19,184	R
1945.....	592	47,372	Less than 1 M	\$171	1.11	3,961	T
1946.....	688	82,696			3.91	15,266	S

^a Less than 0.25 M.

Organization of Domestic Industry

The American Refractories Institute in 1942 listed 179 refractory manufacturers with plants in 33 states. A considerable portion of the total output is contributed by large corporations, roughly a score of which are capitalized at \$1,000,000 or more. A great many plants make only clay firebrick, occasionally adding certain allied fire-clay products, such as special shapes, refractory mortar, and plastic material; quite commonly, however, several brands of firebrick are made in the same plant, varying in composition or in process of manufacture (dry-press, hand-molded or other). Silica brick occasionally are made in the same plant with fire-clay products but more often in a separate plant, although most of the production is furnished by companies that also produce clay brick. Magnesite and chrome brick are generally made in the same plant whereas silicon-carbide brick are often made along with ordinary firebrick.

At least 20 companies operate two or more plants each, and three companies operate 10 or more plants each. Many plants that once were

TABLE 13—Exports of Refractories from the United States

Year	Fire-clay Brick		Silica Brick		Chrome Brick		Magnesite Brick		All Others		Grand Total Value All Refractories
	Thou- sands	Value	Thou- sands	Value	Short Tons	Value	Short Tons	Value	Short Tons	Value	
1931.....	17,526	\$ 831,691	3,102	\$ 281,901	a	a	a	a	7,519	\$ 684,753	\$ 1,798,345
1932.....	7,551	464,727	2,368	183,349	a	a	a	a	4,269	355,824	1,003,900
1933.....	8,928	530,745	3,238	239,166	a	a	a	a	5,611	535,011	1,304,922
1934.....	16,526	1,004,846	4,426	383,294	a	a	a	a	9,178	1,052,108	2,440,248
1935.....	16,037	1,092,520	4,346	390,639	a	a	a	a	10,349	976,110	2,459,269
1936.....	21,225	1,301,283	5,748	466,700	1,960	\$104,170	7,426	\$ 638,101	11,363	661,084	3,161,338
1937.....	26,929	1,849,166	9,911	838,241	2,774	150,425	9,782	806,783	14,420	806,544	4,451,159
1938.....	17,203	1,285,984	5,480	449,807	1,335	78,829	8,017	681,335	13,834	707,433	3,203,388
1939.....	25,237	1,711,470	6,061	453,365	2,871	159,365	11,469	930,517	15,709	875,837	4,130,564
1940.....	33,790	2,242,185	7,632	610,916	4,485	260,221	14,210	1,176,980	18,250	1,030,245	5,320,547
1941.....	60,110	3,569,772	13,317	1,014,360	5,566	377,980	16,141	1,442,270	25,764	1,400,755	7,805,336
1942.....	106,622	4,056,773	17,325	1,862,679	7,432	536,087	15,479	1,513,827	35,221	1,695,365	9,664,731
1943.....	54,331	4,095,682	12,650	1,333,525	7,431	495,733	14,496	1,411,461	49,229	2,626,330	9,962,731
1944.....	45,683	3,537,640	13,895	1,144,340	11,003	771,149	12,491	1,230,620	38,208	2,404,029	9,087,778
1945.....	44,987	3,581,441	9,645	855,336	8,701	648,498	9,243	856,830	24,984	1,773,021	7,715,176
1946.....	55,544	4,996,846	12,593	1,317,388	11,576	847,487	13,253	1,165,515	32,845	2,773,732	11,100,968

^a Not listed separately.

TABLE 14—Prices of Fire-clay Brick, Silica Brick, Chrome Brick and Magnesite Brick F.O.B. Plants, United States, 1922-1947^a

Year	Fire-clay Brick, per Thousand ^b				Silica Brick, per Thousand		Chrome Brick per Short Ton		Magnesite Brick per Short Ton	
	High Duty		Intermediate Duty		Pennsylvania					
	High	Low	High	Low	High	Low	High	Low	High	Low
1922..	43 @ 46	32 @ 46	39 @ 41	28	45 @ 53	28	50 @ 55	40	75-80	52 @ 55
1924..	42 @ 45	40 @ 43	35 @ 38	33 @ 37	50	33	50	45 @ 47	65 @ 68	65
1929..	43 @ 46	43 @ 46	35 @ 38	35 @ 38	43	43	45	45	65	65
1932..	40	35	32 @ 38	25 @ 30	40	35	45	42.50	65	61.50
1935..	45	45	40	40	45	45	45	45	65	65
1938..	51.30	47.50	46.55	42.75	51.30	47.50	49	47	69	67
1939..	47.50	47.50	42.75	42.75	47.50	47.50	47	47	67	67
1940..	47.50	47.50	42.75	42.75	47.50	47.50	50	47	72	67
1941..	51.30	47.50	46.55	42.75	51.30	47.50	54	50	76	72
1942..	51.30	51.30	46.55	46.55	51.30	51.30	54	54	76	76
1943..	51.30	51.30	46.55	46.50	51.30	51.30	54	54	76	76
1944..	51.30	51.30	46.50	46.50	51.30	51.30	54	54	76	76
1945..	54.40	51.30	49.35	46.50	54.40	51.30	54	54	76	76
1946..	65.00	54.40	59.00	49.35	65.00	54.40	54	54	76	76
1947 ^c	70.00	65.00	64.00	59.00	70.00	65.00	59	54	81	76

^a 1922 to 1935, *Engineering and Mining Journal*; 1938 to 1947, *Steel Magazine*.^b Pennsylvania, Kentucky.^c Through Nov. 24, 1947.

operated independently have been absorbed by other companies, and there is a marked tendency toward developing larger productive units. Despite the marked progress in horizontal consolidation, the number and complicated system of individual brand names has not been correspondingly simplified. Firebrick, all rendering essentially the same type of service, are designated by probably 500 different brand names.

Imports and Exports

Imports—The imports of firebrick and other refractories have been relatively small and in recent years have been growing smaller as certain qualities of highly refractory fire-clay brick formerly imported from Great Britain have been displaced by suitable domestic brick. Whereas both dead-burned magnesite and chrome ore are imported extensively into the United States, magnesite brick and chrome brick are made in this country in sufficient amount to supply the entire domestic demand and a surplus for export.

Rates of Duty—Under the General Agreement on Tariff and Trade signed at Geneva on Oct. 30, 1947, magnesite brick are dutiable at $\frac{3}{4}\%$

per pound and 5 pct ad valorem, while chrome brick and all fire-clay brick and other firebrick not especially provided for are dutiable at 6.25 pct ad valorem. The original rates in the Tariff Act of 1930 and also in the 1922 Act were $\frac{3}{4}\phi$ plus 10 pct and 25 pct, respectively.

Exports—Refractories, chiefly fire-clay brick, valued at one million dollars and more annually were exported from the United States before 1914. During the first World War foreign orders increased enormously and continued on a greatly expanded scale until about 1921. During the period 1942 to 1946, the aggregate value of the exports of firebrick and refractory shapes has averaged around \$9,000,000 a year. The large increase in exports in recent years is due to the effects of World War II.

Canada has always been the chief foreign market for American refractories and the bulk of the remaining exports has gone to Latin American countries. Shipments to Europe prior to World War II never amounted to more than a small quantity. Subsequently, they have increased considerably but probably only temporarily.

PRICES

Prices on refractories are on a basis of either per thousand of standard 9-in. brick or per short ton of standard 9-in. brick. For sizes and shapes other than the standard 9-in. brick the base price is subject to extra charge. The amount of the "extra" depends upon the extent to which the size or shape differs from the standard and the subsequent increase in manufacturing cost. Sales are predominately in the standard sizes. A fairly good idea of the trend of prices over a period of years is afforded by the data given in Table 14, showing quoted prices since 1922. These data show the prices on fire-clay, silica, chrome and magnesite brick from the major producing areas. Prices differ somewhat in minor producing areas and commonly are slightly higher, as local conditions may result in higher manufacturing cost. A typical case is that of silica brick produced in Illinois and Indiana. The price is higher than silica brick from Pennsylvania because of the higher cost of obtaining and processing the raw material. Silica brick produced in Utah and California are higher in price than those produced in Illinois and Indiana; high-duty fire-clay brick produced in New Jersey and California are higher in price than high-duty fire-clay brick produced in Pennsylvania, Illinois, Missouri, Kentucky, Texas, Alabama and Georgia.

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CHAPTER 40

SALT

By W. C. PHALEN*

SALT, or sodium chloride, has been known and used from the very earliest times. Because it is one of the essential, primary human needs, the history of its production goes back to the beginnings of human history. It is mentioned in both the Old and the New Testament, at least 24 times. In Cruden's Complete Concordance, it is stated that salt was used as an antidote to the effect of the heat of the climate on animal food and also in the sacrifices. They had an inexhaustible and ready supply of it on the southern shores of the Salt Sea, now called the Dead Sea. Salt symbolized hospitality, durability, purity, and other attributes. To eat the King's salt was to acknowledge fidelity to him. To eat bread and salt together was to make an unbreakable league of friendship. Jewish law commanded the people to season the meat offering with salt.

In those early days, a very impure mixture of salt and clay or shale was used in places from which the salt was extracted with water, leaving a residue of clay or mud. This mud contained some salt and was used either directly for fertilizer or spread on the manure pile, where, after prolonged exposure, in the presence of nitrogenous matter, some sodium nitrate was formed. Hence the biblical expression: "Salt is good; but if the salt has lost his savour, wherewith shall it be seasoned? It is neither fit for the land, nor yet for the dung hill; but men cast it out." (Luke 14: 34-35.)

Because salt is essential to human wellbeing, it has been and still is a favorite basis for taxation and government monopoly and much of the fight for political and economic freedom at times has been waged over production of salt. Where such production has been a government monopoly, it has been a source of both power and unrest.

Salt and its derivatives have found so many uses that touch human existence closely that it may well be considered among the most essential raw materials. The statement has been made that there are 1400 uses. Its use in the chemical industry and the rapidity with which the uses of chlorine and derivatives containing chlorine have expanded need only be indicated to emphasize this fact.

* Consulting Engineer, Washington, D. C.

PROPERTIES

Pure salt is known to the mineralogists as halite. It contains by weight 39.34 pct sodium and 60.66 pct chlorine. It is rather brittle and has a conchoidal (shell-like) fracture. Hardness is 2.5. Specific gravity ranges from 2.1 to 2.6, that of the pure crystals being about 2.17 (135 lb to the cubic foot). Its index of refraction is 1.5442. It is highly diathermous. Electricity, in strong current, will decompose it into its elements. It is translucent or transparent. Luster is vitreous. It is plastic under great pressure, a quality of tremendous import, as will be shown later in the paragraphs on Origin.

The mineral halite is isometric in crystal form. As rock salt, its most common form in nature aside from its occurrence in solution in sea water, it has a coarse, granular to compact structure. When it crystallizes from concentrated solution, it forms cubes, which commonly are distorted or joined in such a way as to form hopper-shaped crystals. Masses with cubical cleavage are fairly common but the fibrous variety and the stalactitic forms are much less so.

Halite is colorless when pure, but pure natural mineral is seldom found. Impurities, chief among which are the common iron oxides, impart to salt different shades of yellow, orange, brown, pink, or red. The peculiar red, brown, or pink tinge observed in some solar-evaporated salt is considered to be due to tiny organisms. The blue mottlings sometimes observed are thought to be due to the presence of colloidal sodium, but this has not been confirmed. These different tints are responsible for the varying degrees of translucence observed in salt.

Salt is readily soluble in water; and its degree of solubility at 100°C is but slightly greater than that at 0°C. This fact has a very important bearing on the cheap production of artificial brine, from which so much evaporated salt is made and which enters so largely into the chemical industry. The characteristic taste of salt is known to all.

COMPOSITION

Analyses of rock salt mined and marketed in the United States and in other countries indicate, in general, a product with high degree of purity, as Table 1 shows. The principal impurity is calcium sulphate plus smaller quantities of the chlorides and/or sulphates of calcium, magnesium, and potassium. As a general rule, the better grades of rock salt contain fewer impurities than do the natural brines and the former generally are devoid of the larger quantities of calcium and magnesium chlorides and the bromine and iodine compounds found in the natural brines. In a particular series of salt strata, obviously only the whitest and purest bed would be selected for a mining operation, so that the analyses in Table 1 would be selective as to purity and would not in-

dicates what might be present throughout a given bed or beds in a salt series or formation. It is believed, based on observation, that even in a given ordinary sedimentary bed all gradations may be present from the barren rock to the pure salt.

TABLE 1—*Composition of Rock Salt*
PERCENTAGES

Analysis No. ^a	1	2	3	4	5	6	7	8	9	10
NaCl.....	98.35	96.44	98.46	98.10	97.23	99.14	99.63	99.00	98.86	95.77
CaSO ₄	0.68	1.60	tr	1.14	1.65	0.17	0.24	0.28		1.62
CaCl ₂		0.23		0.18	0.08	0.03				
MgCl ₂			0.19	0.39		0.02		0.13		0.08
Na ₂ SO ₄	0.48					none			0.57	
MgSO ₄	0.49		1.25			none	0.30			
KCl.....	tr	0.31	tr	0.19						tr
R ₂ O ₃					0.03	none	tr			
H ₂ O.....							0.04		0.08	1.23
Org. matter.....						0.01				
Insoluble.....		1.07			1.01	0.64		0.65		2.20
	100.00	99.65	99.90	100.00	100.00	100.01	100.21	100.06	99.51	99.90

^a These analyses were gathered from miscellaneous sources, mainly official. The numbers indicate:

1. Livingston County, New York.
2. Natrium, Marshall County, West Virginia. This is an analysis of a selected sample, from a depth of 6818 to 6828 ft, Defense Plant Corporation No. 1 well. Most of the rock-salt cores from this well run lower in sodium chloride than this one.
3. Near Detroit, Michigan.
4. Kanopolis, Kansas.
5. Winn Parish, Louisiana.
6. Avery Island, Iberia Parish, Louisiana.
7. Malagash, Nova Scotia.
8. Northwich, England. The best of 120 samples from the bottom bed, Adelaide mine.
9. Mayo mines, salt range of the Punjab, India.
10. Triassic salt, Djebel Hadifa, Tunis, Africa.

The analyses in Table 1 indicate in a very general way the purity of commercial or mined rock salt at a few places. However, where salt is removed by solution, the method that accounts for the larger production, the selection of the bed is of smaller consequence, because only the soluble terrane is removed and this consists mostly of sodium chloride and as much calcium sulphate as a normally saturated brine carries in solution. The chlorides of calcium, magnesium, and potash in general are present only in very small quantity in most rock-salt deposits and, consequently, in the brine resulting from their solution. With the naturally occurring brines (connate brines) the picture is completely reversed.

Although sulphate of lime and the different chlorides of calcium, magnesium, and potassium occur in minor quantities in solution of dissolved rock salt that are to be used in the marketed evaporated product, yet the greatest possible attention is given to their elimination; because the evaporated product goes into the table and dairy market, where flavor and purity, as well as form, type, and grade are of prime importance. Grainer and vacuum-pan salt are the principal types made from artificial brine and their uses are so varied that they can be indicated only broadly. Grain or flake salt is often preferred for salting fish, curing ham and bacon, treating pretzels, curing and treating sausage casings, and in other food industries. It is used on the farm and in curing hides and skins. Vacuum-pan salt carefully graded is used for processing self-rising flour, baking bread, pastries, making butter and cheese, pickling olives, cucumbers, fish, canning fruits and vegetables, and in preserving and packing meats. Large quantities are used on the farm, in making textiles, and in a host of other ways.

In the removal of these impurities to make high-grade salt, the extensive use of chemicals is not always economical unless the products are to be used in the food industry, where they can command a fairly good price. It can be stated, however, that the salt that goes into the food industry is of very high grade and competition is one of the main regulating factors. Generally speaking, the flaked grainer salt, or "flake" salt, going into butter and cheese contains in excess of 99 pct sodium chloride and the calcium and magnesium chloride are almost entirely absent.

In contrast with the analyses of rock salt and of the artificial brines made by dissolving it, a few analyses are given (Table 2) of natural brines or bitterns, showing how markedly they differ with respect to their content of the chlorides of the alkaline earth metals and the almost complete absence of sulphates. These natural brines are the basis of an important salt industry, and are also sources of bromine, iodine, and the mixed chloride of calcium and magnesium.

In a rather recent publication,²¹ chemical analyses of Kansas oil-field brines show that the brines, irrespective of the oil fields or horizons from which they come, are much alike in their dissolved chemical constituents but differ materially in concentration. The analyses show that of all the dissolved chemical constituents contained in the brines, chlorides of sodium and calcium greatly predominate (Table 3). Magnesium is next in importance quantitatively. Other elements present that occur in much smaller quantities are bromine, iodine, aluminum, iron, and potassium. Magnesium, of all the chemical constituents contained in the brines, is of considerable interest. It occurs in sufficient quantity to offer possibilities of commercial extraction under war conditions at least. Other ingredients, as sodium and calcium, occur in far greater quantity than magnesium but their extraction from Kansas

TABLE 2—*Analyses of Some Natural Brines*

Analysis No. ^a	1	2	3	4
Depth of well, ft.....	1,200	3,640	3,470	3,665
Specific gravity.....	1.223	1.133	1.207	1.230
Bromine, pct.....	0.14	0.03	0.133	0.138
Percentage by Weight of Different Ingredients				
CaCl ₂	8.77	2.95	8.56	11.10
MgCl ₂	2.80	0.83	2.57	2.70
NaCl.....	14.92	12.75	12.47	12.50
KCl.....	0.17	0.22	0.41	
MgBr ₂	0.16	0.035	0.15	0.16
CaSO ₄	0.016	tr		
Total.....	26.836	16.785	24.16	26.46
Water by difference.....	73.164	83.214	75.84	73.54
Grams per Liter				
CaCl ₂	107.26	33.42	103.32	136.53
MgCl ₂	34.24	9.40	31.02	33.21
NaCl.....	182.47	144.46	150.51	153.75
KCl.....	2.08	2.49	4.95	
MgBr ₂	1.96	0.40	1.81	1.97
CaSO ₄	0.20	tr		
I ₂		0.01		
Total.....	328.21	190.18	291.61	325.46
Water by difference.....	894.79	942.82	915.39	904.54
Br, gpl.....	1.70	0.35	1.60	1.69

^a 1. Midland, Michigan; Bureau of Mines *Bull.* 146, 82-83.2. Texaco Salt Products Co., West Tulsa, Okla.; *Jnl. Eng. and Ind. Chem.* (1932) **24**, 547. Plant now closed.3. Sec. 23, T13N., R1W, Midland County, Michigan, Porter oil field; Mich. Geol. Survey *Pub.* 38, Geol. Ser. 32, Oil and Gas Fields of Michigan, 1933, 190. Dundee formation.4. Sec. 14, T15N, R9W, Mecosta County, Michigan; *ibid.* Dundee formation.TABLE 3—*Dissolved Chemical Constituents of Kansas Oil-field Brines*

Chemical Constituents	Range, Milligrams per Liter	Chemical Constituents	Range, Milligrams per Liter
Total solids.....	17,880-228,320	Bromide.....	0-425
Chloride.....	10,729-142,547	Iodide.....	0-8
Sodium.....	9,200-68,700	Sulphate.....	0-2,800
Calcium.....	246-7,900	Aluminum.....	0-781
Magnesium.....	153-3,960	Iron.....	0-15
Bicarbonate.....	12-869		

brines probably would be unwarranted and unprofitable. Studies show that certain formations are invariably higher in magnesium content than brines coming from other "pay zones" or oil-producing formations.

Sea-water Bitterns

Commercial grades of magnesia are produced in large quantities from sea-water bitterns²² at the plant of the Westvaco Chlorine Products Corporation at Newark, California. Though a variety of special conditions that surround this operation make its functioning and its economic status somewhat different from those of any other synthetic magnesia unit likely to be developed, in the United States at least, nevertheless the commercially proved nature of the operation and numerous interesting features surrounding it make it worthy of note.

In this operation, bitterns remaining after salt has been recovered from the sea water by solar evaporation, at plants in the San Francisco area, are pumped to large storage ponds, adjacent to Westvaco's Newark plant. These bitterns contain: NaCl, 12.5 to 16.0 pct; $MgCl_2$, 6.0 to 8.7; $MgSO_4$, 4.2 to 6.1; KCl, 1.4 to 1.9; $MgBr_2$, 0.14 to 0.20; total, 24.24 to 32.90.

Currently the storage ponds at Newark have a capacity of 200 million gallons of bittern averaging 28° to 30°Be.

MODE OF OCCURRENCE

Salt occurs: (1) in solid form and (2) in solution.

Rock Salt

The common type occurring in solid form is rock salt. This form of salt, untreated or dissolved, is the most important source of the prepared or commercial article and also of the brine that goes into the chemical industry. Rock salt occurs in at least two widely different structural forms; namely, as (1) beds or lenses, and (2) "salt structures." The latter is a broadly comprehensive term, which covers the great variety of forms not classifiable as bedded deposits, such as bosses, plugs, ridges, or domes, as they are called along the Gulf Coast of Mississippi, Louisiana, Texas, and Mexico. Although salt domes are associated with sedimentary rocks, they differ in origin and form from the common bedded, stratified, or lenticular types.

The occurrence of rock-salt beds or lenses associated with the common types of sedimentary rocks of nearly all geologic ages down to the present is well known. In addition to the commonly stratified rocks associated with rock salt, such as shale or sandstone, and the calcareous types, such as dolomite and limestone, it is interbedded with other saline minerals, as gypsum, anhydrite, and the potash and magnesium saline in various parts of the world, notably in Germany, France, Spain,

Poland, Russia, and the United States. Single beds or groups of beds aggregating hundreds of feet in thickness are not uncommon.

The areal extent of such rock-salt beds is immense, as in the great Permian Basin, covering parts of Kansas, Colorado, Oklahoma, Texas, and New Mexico, whose area is reported to be, in round numbers, about 100,000 square miles. We are not accustomed to thinking in such terms of areal extent in the eastern part of the United States but it is reported that the approximate area underlain by rock salt in New York, Ohio, Michigan, Pennsylvania, West Virginia, and Ontario aggregates 69,600 square miles.¹² In addition to this, there is almost certainly rock salt beneath large but unknown areas of Lakes Erie, Huron and Michigan. It is of significance that Martens¹² states the probability that the salt deposits of New York, Pennsylvania and Ohio are connected with those of Michigan and Ontario by a broad strip under Lake Erie and across the saddle of the northern extension of the Cincinnati (geological) arch in the vicinity of Lake St. Clair.

A revealing estimate of the extent of the Louann salt has recently been made in a report prepared by the Shreveport Geological Society.⁸ The Louann Salt is the name applied to the source bed of salt of the domes in Texas, Louisiana, and Mississippi, and which is reached in the deep wells drilled in northeast Texas, south Arkansas, north Louisiana, central Mississippi, and southwest Alabama. The estimate of the extent of the Louann Salt Basin is based on the assumption that the known salt domes of northeast and Gulf Coast Texas, Louisiana, Mississippi, and Alabama derive their salt from this common source. If the Louann Salt is continuous from Arkansas to the Texas-Louisiana-Mississippi Gulf Coast, which possibility seems to be indicated, a minimum estimate of 180,000 square miles underlain by it appears to be a reasonable figure—and the original maximum area may greatly exceed this figure.

Great domes, bosses, stocks, plugs, or ridges of rock salt, differing genetically and structurally from the ordinary type of bedded deposits, are known to occur in areas of sedimentary rocks throughout the world. Such occurrences have been referred to as "salt structures"²; and they occur not only along or near the Gulf of Mexico, in Mississippi, Louisiana, Texas, and Mexico, but also in Colorado and Utah, and in many foreign countries—Colombia, Germany, Spain, Alsace, Rumania, Egypt, Algeria, Morocco, Persia, and the Soviet Republic, especially in the Emba region between the south end of the Urals and the Caspian Sea. Probably the occurrence of rock salt at Malagash, Nova Scotia, belongs in this classification. As the occurrences along the coast of the Gulf of Mexico, both in the United States and in Mexico, are of the domal, plug, or boss type, they are appropriately referred to as domes.^{25,26}

In certain countries, especially in Europe, salt occurrences are intimately connected with those of potash salts, and indeed, from an economic viewpoint, as in Germany, Alsace and Spain, the latter are of far greater economic importance.

Much rock salt is intimately mixed with anhydrite, gypsum, and small quantities of the chlorides of calcium and magnesium. Practically all of the commercial deposits of potash salts are mixtures of rock salt and potash salts in varying quantity. Our New Mexico potash salts are an example. Taylor²⁶ lists 17 minerals in the water-insoluble residues of the salt plugs that he studied plus potash salts and quartz sand, and he says that data are available from only 20 localities, chiefly in Louisiana. Taylor also lists from Boeke²⁶ 26 minerals from the water-insoluble residues of the German Zechstein salt deposits. In addition to saline minerals, rock salt usually contains a mixture of rock particles, such as shale, limestone, dolomite, sandstone; and all gradations occur from practically pure salt at one end of the scale to barren rock at the other.

It has been generally believed that salt in the Gulf Coast domes is of purer quality than the ordinary bedded variety, and it may be in certain specific cases. It is known, however, that anhydrite and/or gypsum are abundant in dome salt and that potash salts in small quantity are reported from different domes in Texas and Louisiana. These constituents together with the residual minerals found in the cap rock, which must have come from the original rock salt itself, indicate that the concept of dome salt being almost pure salt has become quite untenable⁵ and that the figure of 5 to 10 pct impurities may not be too high; in fact, such percentages seem probable because it is now supposed that dome salt has come from originally bedded deposits. As time goes on, and a more intimate knowledge is obtained of salt structures throughout the world, probably it will be found that, as far as admixed foreign matter is concerned, the two types are quite comparable.

Salt in Solution

Ocean water is the familiar example of salt and other salines in solution but such salines occur also in the waters of inland seas and lakes without natural outlets, scattered through all parts of the world. Great Salt Lake, Utah, is the outstanding example in the United States, but similar examples occur in Asia, Africa, Australia, and, in fact, in all lands where desert conditions prevail.

In the form of connate or natural brines, salt is widely distributed in porous sedimentary rocks and sometimes comes to the surface as brine springs or is discovered in drilling oil and gas wells. In certain places, soils or porous glacial deposits are impregnated with natural brine. This type of occurrence has been and still is a minor source of salt, magnesium, and calcium chlorides, and bromine, especially along

Ohio and Kanawha Rivers, both in Ohio and in West Virginia. In Michigan, such brines long ago became the basis of an important chemical industry in the Midland and Saginaw Valley districts and are still used on a considerable scale in this and other parts of the lower peninsula. In Southern California, such brines have become sources of iodine. The residual bitters of the solar salt industry bordering San Francisco Bay are used on an important scale for commercial grades of magnesia.²² Perhaps the salt at Searles Lake might appropriately be noted here as well as the brine-saturated saline deposits of western Utah, which contain potash salts as well. At present the Utah area is being worked for the potash salts only but annually a considerable tonnage of crude by-product salt results from the process of extracting the potash. Recent reports on Kansas oil-field brines,²¹ which show large content of magnesium and other salines, are of considerable interest.

ORIGIN OF ROCK SALT

The German geologists have done considerable speculating on the origin of salines during the past 10 years. This naturally follows from the conspicuous importance of this class of mineral deposits in their own country. Their interest, however, is not confined to Germany, but has covered the whole field. On one point, all who have studied the subject can and do agree; namely, that the immediate original source of all salines is the ocean itself.

In two sections devoted respectively to general and regional geology, Ernst Fulda³ presents a brief summary of salt resources of the world, along with a much more detailed summary of the German occurrences; also a good statement of his own and other geologists' views on the nature and origin of salt deposits and some interesting notes on the history of salt production and the scientific investigation of salt deposits. As a result of the collaboration of N. Polutoff, the description of Russian occurrences is fairly detailed and is perhaps the best account to be found in any non-Russian language. The occurrences in other countries, particularly non-European, are described less adequately.^{3,18}

Fulda gives an excellent summary of the data regarding salt minerals and their properties, the rocks with which they occur, the modern view as to the precipitation of the various salts from solution, the behavior of salt under high pressure, the radioactive properties of salt solutions, and the origin of salt deposits. Like many other writers, he finds the bar theory of Ochsenius¹⁷ attractive but not entirely convincing, and most other theories, including those of Walther¹⁶ and Fulda himself, scarcely better. He concludes this part of his discussion with the presentation of a modern theory, which seems to answer all our needs if one can believe it. This is the great Tidal Flood Theory of Martin Wilfarth.^{4,31}

To Fulda, however, who is the author of one of the theories of the origin of salt deposits that Wilfarth specifically attacked, it now seems that the accumulation of great salt masses is better explained by the aid of the Great Tidal Flood Theory than by his own or any other of the earlier theories.

This new theory rests in part on the idea that the old earth split up long ago into two parts; one of them, the present earth, and the other, the moon. The distance between the two fragments has gradually increased from nothing worth mentioning to approximately 240,000 miles. At the same time, there has been a gradual lessening of the height of ocean tides. In the early days, late Paleozoic for instance, the tides were recurrently large enough to flood vast areas of low-lying land adjacent to the shore; to plane off any remaining irregularities left by unfinished stream erosion; and to pile up extensive masses of sand like the Bundsandstein and give them the features that have led to endless doubt and disagreement as to their marine or nonmarine origin; and to flood subsiding inland basins repeatedly with volumes of sea water that remained to evaporate and deposit their content of salt during the dry periods that intervened between tidal floods. Strange as it may seem, this theory is the only one, apparently, that accounts satisfactorily for the great salt deposits of Germany.

From the foregoing paragraphs, it will be clear that as a discussion of modern concepts of salt geology and of the salt deposits of Germany and Russia, Fulda's volume is of great value. With reference to the tectonic relations of salt deposits, the works of Stille and Lotze,^{11,19} who attack the problems from a somewhat different angle and discuss them in much greater detail, should also be examined. As far as the salt deposits found outside Germany and Russia are concerned, Fulda's summary will serve for most of us, and his references will permit others to find the more expensive accounts they may need. In Lotze's work, North American salt deposits are summarized in about 60 pages. Lotze believes that similar relationships of salt deposits to regional structure prevail in North America and Europe.

The foregoing notes on the work of Fulda, Wilfarth, and Lotze are from the reviews of R. D. Reed^{18,19} and are, as given, practically verbatim quotations. Works by American writers—Grabau, Alling, Branson—will not be discussed here because they were noted in the first edition (AIME, 1937). The references in the bibliography will enable the student to pursue the subject as far as he likes.

An entirely different explanation is forthcoming with reference to the "salt structures" of the world, more especially the domes of the Gulf Coast states. The theory of the formation of these salt domes by the plastic flowage of sedimentary salt under pressure has now come to be generally accepted by men who have studied the subject most intensively.

R. D. Shrewsbury²³ likens the flow of salt to the upward flow of lava and believes that the salt domes of the Gulf Coast of the United States are only a small segment of a system of similar structures, most of which are now submerged but which are distributed about an area of subsidence that has persisted throughout a vast expanse of geologic time. If the center of this area could be located, a picture of the salt-dome system could be mapped. Certain of the illustrations accompanying his paper are of interest.

L. L. Nettleton¹⁵ has presented a theory of salt-dome formation and illustrated it with a model that indicates: (1) that the motive force causing salt uplift in simple domes is essentially the gravitational force resulting from the fact that the density of the salt is less than that of the surrounding sediments, and (2) that both salt and sediments behave essentially as highly viscous fluids. His latest contribution, in 1943, considers the experimental and theoretical work, largely by others, which has a bearing on this fluid-mechanical theory. All the work done serves to confirm the general hypothesis that salt-dome formation is largely a fluid-mechanical process.

In a recent contribution, Bailey Willis³² assigns the formation of Gulf Coast salt domes to the artesian flowage of brine but warns that because of the scarcity of data available positive assumptions are dangerous.

Data indicate that the base of the salt cores of some of the Gulf Coastal domes lies in some places at depths of 17,000 to 20,000 ft, as in the Houston district, Texas.^{1,2}

DISTRIBUTION OF DEPOSITS²⁸

Fortunately for mankind, salt is widely distributed and those countries bordering on the sea are particularly well off in their assurance of an endless supply. A list of countries where salt is found or produced includes practically every political division on earth. In compiling the information on foreign countries, the author has depended on the voluminous data gathered by the U. S. Bureau of Mines and published in its Mineral Trade Notes.

United States

The people of the United States are particularly fortunate that salt is so widely distributed and is so close to the largest centers of population that it can be obtained cheaply in the forms that are best adapted to the consuming market or can be converted readily into those basic chemicals so essential and useful to our civilized mode of life. In the northeast part of the United States, extensive salt deposits are found as far east as Central New York and similar rock-salt formations are in Pennsylvania, Ohio, and West Virginia. It is more than likely that this same

series of Silurian Salina salt beds is connected under the Great Lakes with the salt beds of the same age in Ontario and Michigan. Other states in which rock salt is now known to occur are Alabama, Arizona, Arkansas, California, Colorado, Idaho, Kansas, Louisiana, Mississippi, Montana, Nebraska, Nevada, New Mexico, Oklahoma, Texas, Utah, Virginia, and Wyoming. As time goes on, other states doubtless will be added to the list. Salt occurrences often are segregated within groups of adjoining states, as in the northeast group already named. Along the Gulf Coast, Alabama, Mississippi, Louisiana, and Texas form a group where certain of the salt deposits fall into the category of salt domes. We may expect south Georgia and Florida to be added to the list at some future time. In the West or Southwest, Kansas, Colorado, Oklahoma, Texas, and New Mexico form a natural group of states underlain in part by an immense body of Permian salt beds, which in New Mexico contain also important deposits of potash salts.

Rock salt, the main dependence of the industry, is well scattered over this country, but is lacking in certain large areas where consumption is great. For example, it is not present in any of the New England states though it occurs only 100 miles east of Maine, in New Brunswick. In the latter province, a salt basin was found in 1921 during drilling for oil near Coutreau, south of Moncton, near the Petit Codiac River. The absence of salt in New England enables foreign salt to compete along the coast, especially in the fishing industry. Except for a small local deposit in southwest Virginia, which forms the basis of an alkali industry, no rock salt is known to occur south of the Ohio and east of the Mississippi Rivers, except in the Gulf Coast states. In the Mississippi River Valley, north of Arkansas and Louisiana, there is a vast area where no rock salt has been found to date. In the northwestern coastal states, no important salt beds have been found, as far as the writer is aware.

Sea water, saline lake water, and connate or fossil brine have each become the basis of important salt and chemical industries in this country. Sea water is the basis of the large solar salt business on San Francisco Bay, Monterey Bay, and near Los Angeles and San Diego; and in recent years on San Francisco Bay, the bitterns remaining after the salt has been extracted have become a source of magnesium compounds. The water of Great Salt Lake is solar evaporated and produces an important quantity of salt.

Connate brine has long been the source of a considerable salt business along the Ohio River, in Ohio, and the Kanawha River in West Virginia. Saginaw Valley, Michigan, was and still is the site of a considerable salt industry. At Midland, connate brines were the starting point of a large chemical industry, involving the manufacture not only of salt but of bromine, bromides, and salts of calcium and magnesium.

In Oklahoma and Texas, natural brines have been utilized and certain natural brines at Sea Beach and Compton, in southern California, are utilized for their content of iodine. Such sources of salines have come to have great possibilities, especially with reference to their magnesium content, and their study is being pursued rather intensively.^{21,24}

Canada

Salt has been produced recently in Canada by nine different concerns at eight different places. Rock salt mined at Malagash, Nova Scotia, is used but most of the salt is recovered from brine. A drilling campaign undertaken by the Nova Scotia Department of Mines gave evidence of important salt beds in the vicinity of Nappan, near Amherst, Cumberland County. A company organized to manufacture salt was expected to be operating early in 1947.

Drilling for oil during the summer of 1944, near Mabou, Inverness County, Cape Breton, exposed several beds of salt in a deep well, which went to about 7000 ft. Deep salt has also been found on Prince Edward Island.

In New Brunswick, an important salt basin was discovered during drilling near Moncton. Many million tons of salt await development in the vicinity of Coutreau.

In 1945, an important discovery of rock salt was made 14 miles south of Vermilion, Alberta. The strike was made at 3400 ft and the bed has a thickness of 400 ft. The Waterways salt bed, in the Fort McMurray district, which is now being worked, is 200 ft thick at a depth of 700 ft. Natural gas is available at Vermilion and will be important in the development of a salt industry.

In Manitoba, salt is being produced from natural brine at Neepawa, while rock salt is reported in drilling near Unity, Saskatchewan. Potash salts have been reported recently from that vicinity.

An important rock-salt operation, the only one in Canada, is at Malagash, Nova Scotia. In Ontario, quantities of salt and other sodium chemicals are produced from the extensive deposits in the southern part of the province in Essex, Lambton, and Huron Counties.

Mexico

Salt is widely scattered over Mexico, both as rock salt and in solution in lakes, springs, and other waters. It is extracted by solar evaporation in many places along the coast. An alphabetical list of the 22 states where it is known to occur or has been worked is as follows: Lower California, Campeche, Coahuila, Colima, Chiapas, Chihuahua, Federal District, Durango, Hidalgo, Mexico, Michoacan, Nuevo Leon, Oaxaca, Puebla, Ineretaro, San Luis Potosi, Sinaloa, Sonora, Tabasco, Tamaulipas, Yucatan, Zacatecas.

West Indies

Cuba—About 80 pct of the salt consumed in Cuba is supplied by the local industry; the rest is imported, practically all from the United States. The extraction of salt by solar evaporation of sea water has been practiced since the island was discovered. It was not till early in the present century that artificial evaporation was practiced on the island and the "salinas," though probably more sanitary, follow more or less closely very primitive procedures. Cuban salt is available in certain American types; for example, fine table salt, fine salt for cooking purposes and other grades. There are more than 20 salt works in Cuba, of which at least 17 are in operation. There is a consumption tax and also a production tax (large or small), depending on whether the salt is produced on government or private land.

British West Indies—Salt is extracted from sea water by solar evaporation in the Bahamas. Production is about 30,000 net tons yearly. There are salt ponds at Inagua, Raeged Island, Rum Cay, Bight, and Cat Island. The first named is the most important.

On Turks and Caicos Islands, salt production by solar evaporation is the chief industry and goes back to 1678, when it was begun to meet the needs of New England fishermen. The three producing islands are Grand Turk, Salt Cay, and Cockburn. The uniform temperature, which during the day is about 84° to 86° in summer and 75° to 80° in winter, the constant trade winds and low rainfall all contribute to production. In the decade 1930-1940, three grades of salt were exported: (1) coarse, the natural product of the salinas, (2) fishery salt, a grade with a fineness suitable for curing fish, (3) industrial, fine-grained, suitable for dairy and similar purposes. Recent exports include only the first two.

Netherlands West Indies—Salt is produced at Curaçao, Bonaire, and St. Martin. Walled ponds, with an average depth of 3 ft, fill with sea water through artificial canals direct from the sea and are then closed by a dam. After 4 to 6 months evaporation, depending on the rainfall, the salt crop is ready to be reaped.

Dominican Republic—Law No. 1081, Jan. 12, 1946, provides that the Republic shall have exclusive right to extract and manufacture sea salt or rock salt for any purpose whatever. Much salt is evaporated from sea water at Calderas, on the south coast of the Republic. In the southwest, near Cabral, Barahona Province, are the well-known salt hills of the island. They are about 18 km (11 miles) long, of which 14 km (8½ miles) is almost solid salt, stratified in almost vertical lenses. The salt is worked in large opencuts 100 ft high by 100 ft wide and several hundred feet long. The deposit is worked by Salinera Nacional. Total output in a recent year was 12,620 metric tons, of which the mined rock salt

amounted to about 2000 metric tons. The total output is increasing from year to year.

Marine salt is now produced in Haiti in quantity sufficient to supply nearly all the requirements of this Republic, so production tax is now collected.

Central America

Guatemala—The major production of salt in Guatemala is solar salt derived from sea water, but the Indian population prefers salt derived by boiling coastal marine earth. Salt is taxed by the Government. The industry has been beset by controversies in recent years, especially following the revolution of October 1944. The Government issued a decree in August 1940 designed to control production and price of salt. The creation of a salt consortium was provided for and marketing was to be governed by production quotas. It is understood that the Government pool was later dissolved and the industry is now under older laws whereby production and sales have no limits.

South America

Panama—Output of salt in Panama in a very recent year was 11,000 net tons of solar-evaporated sea salt. A Government bank is in charge of output and distribution of the product.

Colombia—Rock-salt deposits are known in five places—Zipaquirá, Nemocon, and Sesquile, in the Department of Cundinamarca, the Cumural y Upin near Restrepo, and San Miguel y Barital, near Medina in Meta Intendency. The latter deposit never has been worked on account of its inaccessibility. Saline springs are worked in four locations. The largest producer among marine salinas is Manare but it is now planned to make Bahía Honda the largest. Some evaporated salt is made in vacuum pans. The deposits at Zipaquirá, Nemocon, and Sesquile are believed to occur in the domal type of deposit. All the salt resources are under Government control.

Venezuela—The salt industry in Venezuela is under Government control and is taxed. Taxes in recent years, however, have been reduced for salt used in curing hides and salting meats, fish and fish products. Production has approximated 25,000 metric tons yearly but may now be considerably above that figure. The basin on the peninsula of Araya, State of Sucre, which at present is the only important source of salt, could produce at least 175,000 metric tons if more ground were provided—a larger supply than the entire country could consume. This unique landlocked basin of nearly 1000 acres lies 12 ft below sea level.

Ecuador—Salt is a Government monopoly in Ecuador and is produced chiefly by solar evaporation close to the shore. The main producing center is on the Santa Elena peninsula, which supplies about 90 pct of the salt. Small fields are at Punta Arenas, Payana, and Chara-

pata. Some rock salt is mined at Salinas, Imbabuba Province, in the mountainous section of the interior, but the output is less than 1 pct of the country's total.

Peru—The salt industry of Peru is a Government monopoly under the Compania Salinera Nacional, a Government organization through which all the salt produced is sold. The salt comes from the "salares" along the coast in the departments of Lima, Piura, Arequipa, and Ancash, which supply about 60 pct of the output, and from beds of rock salt in the departments of Cuzco, Apurimac, Ayacucho, Puno, and Huan Cavelica, which yield about 40 pct of the total output.

Brazil—Brazil had a total of nearly 1000 salt plants, with an output of approximately 700,000 metric tons, in a recent year. Some of the solar salt is of very high grade; from Rio Grande do Norte, for example, it contains 98 pct NaCl, and from Rio de Janeiro, it is 96 pct pure. These are the two most important salt-producing states. Even with this large output, there has been a shortage at times and certain states—for instance, São Paulo—have had to import salt from Argentina or from other states, as Cabo Frio and Rio de Janeiro. The National Salt Institute has agreed to remove the provision restricting production of salt in Rio de Janeiro to the period between September and April, and has asked producers to step up the output to the maximum.

Twelve states contributed to Brazil's salt output in recent years, all of which came from solar evaporation of sea water. No use is made of the residual bitterns.

Rock salt has been encountered in drilling for oil in the vicinity of Maceio, Alagoas, and in the State of Sergipe. The rock salt in both states is said to occur at a depth of about 950 meters, with a thickness of 100 meters. Analysis from a single well near Maceio indicates the salt to be of exceptionally high grade. Up to 1945, there was no utilization of rock salt in Brazil.

Argentina—Salt is produced in Argentina at the rate of about 400,000 metric tons yearly and some 10 pct is exported, largely to Brazil. In Argentina, salt is widely distributed in salt lakes, where it has been concentrated naturally through solar evaporation under arid conditions. These deposits supply local needs but no large works have yet been built except in the southern part of Buenos Aires Province, where an evaporating plant on San Blas Bay recovers salt from brine pumped from a near-by lake. Salt is collected during the dry season along the shores of lakes at Salinas Grandes, on Valdez peninsula, Province of Chubut. A railroad built to the coast facilitates shipments. At San Luis, considerable salt comes from Lake Behedero, about 25 miles south of the city. There are several important salt lakes within easy reach of the railroads, which might be used as sources of salt, notably in the Sierras de Cordoba, in Los Andes, Jujuy, Salta, Buenos Aires, and San Juan.

Chile—Chile produces enough salt for its own need but imports a small quantity of refined salt. Large salt pans occur in the arid districts of northern Chile, notably the Solar Grande in Tarapaca Province. This salar covers 80,000 acres and contains nearly pure salt. A salar at Lagunas is also of importance.

Europe

Rock salt is widely distributed in Europe and the rather recent discovery in Denmark adds this country to the list.

Austria—Salt deposits in Austria, which have been worked since the eighth century, are large and important and reserves are estimated in the hundreds of millions of tons. Deep boreholes have disclosed additional reserves underlying those already known. Principal deposits are at Hallstadt, Bad Ischl, Bad Aussee, all southwest of Linz, also Ebensee, in upper Austria, Hallein near Salzburg, and Halle in the Tyrol. All these are in operation, except possibly that at Hallstadt, which was damaged in the war; and that may now be at work.

Salt is produced by the evaporation of brine; although some rock salt is produced. Salt production is a State monopoly and the salt is sold directly from the State refineries to wholesale dealers, who distribute it to the retailers.

Portugal—Current rate of output of salt in Portugal is about 300,000 metric tons yearly, including rock and sea salt. The rock-salt output is not large. The industry is static and relatively stable, and simple methods of production are used. The fishing industry is the chief consumer but the heavy-chemical industry consumes a considerable amount. Large stocks are said to be on hand.

The industry enjoys considerable freedom from Government control but there is an export license, which may be withheld if the Government considers the domestic supply insufficient.

Spain—Spanish output is approximately 700,000 metric tons per annum. Rock-salt production is important but recently has been relatively static. Production of solar salt along the coast is primitive and the fisheries consume most of it. Heavy chemicals are the next largest consumer. Nearly all the rock salt mined comes from Polanco, Santander Province, and is used in making soda ash and caustic soda in a plant at Barreda.

There is no private or Government monopoly on salt, except for taxation purposes. Special taxes consist of a sales tax, amounting to 100 pct ad valorem, applied to internal consumption only. There is no export duty.

In recent years, salt has been produced from at least 18 provinces. Rock salt comes principally from Santander Province. Alicante and Cadiz are foremost among the producers of solar salt.

Turkey—At present, 62 salt operations are active in Turkey and the annual output is from 250,000 to 275,000 metric tons. All salt-producing facilities are owned and operated by the Government. Sea salt at Camalti, near Izmir, accounts for 75 pct of the output; other operations are mostly small. The Camalti plant, because it can supply salt cheaply and easily to all areas on or near the coast, has an advantage over all other producers. Inland plants can supply their product only locally because of high cost of rail transportation.

Germany—Salt resources are large and widely distributed in Germany. It is mined from thick beds and is evaporated from brine from wells and springs. Extensive deposits are found in Prussia near Hanover, Magdeburg, and Stassfurt, in the Werra district, Thuringia; near Heilbronn, Wurtemberg; in the Rhine Provinces, Braunschweig, Baden, and Bavaria.

Prewar production averaged 3,000,000 metric tons and 800,000 metric tons was exported yearly. During the war years, output reached well over 4,500,000 metric tons and the salt content of the brine used in the alkali industry was said to be as much as 900,000 metric tons yearly.

To make certain that no tax-free salt may be used as edible salt, which is taxed in Germany, a chemical is added, which in no way impairs salt for industrial purposes but makes it unfit to eat.

Denmark—In early June, 1946, a test hole, placed on a gravitational minimum in the Limfjord area of Jutland, about 5 miles north of the town of Holstebro, pierced pure rock salt at 806 ft. The well was carried to a depth of 1517 ft in clear rock salt. In the same way, rock salt has been found at Suldrup, near Aalborg, at the Limfjord. In about 10 other localities in the same area, domes of salt have been indicated by help of geophysical investigations but have not yet been proved by drilling. As Denmark has had to import all its salt, these discoveries are of great importance to the country.

France—Normally, salt production in France, exclusive of that going into soda works, during the recent '40s has averaged between 800,000 and 900,000 metric tons per year (868,000 metric tons in 1942). In the same year, the salt in brine from rock-salt deposits was somewhat less (842,000 metric tons). France has practically inexhaustible supplies of rock salt in the Departments of Meurthe et Moselle, Moselle, Doubs, Haute Saône, in the northeast part of the country; in Jura, in the middle east bordering Switzerland; in Haute Garonne, in the middle southern border of the country, in the Pyrenees, and in Basses Pyrenees and Laudes, in the southwest corner, both bordering on the Atlantic Ocean.

Saltworks abound on the seacoast of the Departments of Bouche du Rhone, Corsica, Gard, Hérault, and Var, on the Mediterranean Sea, and there are some in the Departments of Charente Inférieure, Loire Inférieure, Morbihan and Vendée, on the Atlantic Ocean.

There is no Government monopoly on the salt industry in any of its phases nor does the Government participate in salt production in France. The salt industry is subject to the same fiscal and social regulations as are all other French enterprises.

Balkan Countries—It may be said of the Balkan states—Hungary, Rumania, Bulgaria, Yugoslavia, Czechoslovakia, and others—that there are important reserves of rock salt and some salt is produced by solar evaporation along the seacoasts. Because of the changes in international boundaries, it is difficult to say to which country some of the mines now belong. Taken as a whole, this group of countries produces a great tonnage of salt, some of which goes into the basic chemical industries. In certain countries, the industry continues to be a Government monopoly.

United Kingdom—Salt deposits in the United Kingdom are principally in Cheshire, Worcestershire, and Durham, England, and in Carrickfergus, Ireland. Most important is the Northwich deposit, Cheshire, where the salt horizon is made up of two beds of rock salt, each about 90 ft thick, separated by 40 ft of marl. As the top bed is only 20 ft below the surface, there has been some surface caving. The rock salt averages high in quality, is opaque, and a brownish white color due to admixed earthy material.

A salt union was formed nearly 60 years ago whereby most of the salt producers in England and Ireland banded together in an organization that made it the largest salt proprietor in the world. It is understood that the control is now vested in one of the large chemical concerns that owns the larger share of the salt-manufacturing capacity in the United Kingdom. No Government control is imposed on the salt industry for tax purposes or otherwise.

Italy—In the frequent bombings along the Sicilian coast, the Trapani salt fields, which supplied much solar salt to the Scandinavian countries, did not escape. The plants refining the crude salt employ windmills for power. Salt for export is stored in huge pyramids on the shore.

The Italian Empire suffered other important salt losses when it had to yield its African colonies to the United Nations. About 1940, the East African colonies were exporting annually 250,000 tons of salt, more than Italy itself exported. Most of this went below the Suez Canal and to the Far East. Japan lost its supply of salt from this region when it was occupied by Allied Forces.

Poland—Poland has large resources of rock salt, especially in the former German and Austrian provinces. The most extensive salt-bearing area extends from Dobromil in a southeast direction to the Rumanian border, a distance of 230 km (140 miles) with a width of 20 km (12 miles). In this area, potash salts occur. Reserves are stated to be more than two billion tons.

A third deposit occurs in Silesia, near Rybnik, which also has an

immense reserve. Still another reserve is found to the north, near the western border, which is of Permian age and is believed to be an extension of the vast salt area of Germany.

There was formerly a Government salt monopoly, which may be still in force.

*Soviet Russia*²⁸—Salt is a commodity of which there is a large output and enormous resources in Russia. Recent figures of production are not available but they may be in excess of 5,000,000 metric tons yearly. Imports and exports are negligible. The resources include rock salt, lake salt, and what we would call playa, or dry-lake salt. Total resources of developed salt amount to 1,715,000,000 tons. The largest occurrences of rock salt are in the Orenburg Province (Ilets deposits), the Sverdlovsk Province (Upper Kama and Shunkovo deposits), and the Ukrainian Republic (Artemovski deposit). Immense reserves of rock salt are supposed to comprise the Usol deposit in East Siberia and Khodzha-Munyn deposit in Tadzhik Republic (Central Asia). These are not yet sufficiently prospected to make tonnage estimates.

Resources of lake salt are estimated at 3,540,000,000 tons. The largest commercially exploited sources are: Lake Baskunchak and Lake Elton, the group of Irtysh lakes, and the system of Azov-Black Sea lakes with their practically inexhaustible resources.

The reserves of basin or naturally evaporated salt are likewise unlimited. The largest sources of this type of salt are found in the Crimean peninsula and in the Sverdlovsk Province in the Urals (Solikamsk).

Geologic mapping and prospecting of salt occurrences thus far are insufficient and far from complete. It is to be noted, however, that the geographic distribution of salt deposits in the Soviet Union is very uneven. Alongside of districts rich in salt reserves, as the Aralo-Caspian Basin, there are other areas such as the northern district, the central part of European Russia, and the Far East, which are almost entirely lacking in salt reserves.

Switzerland—After iron ore and coal, rock salt is the most important mineral resource of Switzerland from an economic point of view, as it is the basis of the country's chemical industry. The deposits in the northern part of the country are large enough to meet all requirements for an indefinite period. Production is about 100,000 metric tons yearly.

Asia

Japan—In Japan, the salt industry is and has been badly dislocated as a result of the war and there is a great shortage of salt for all applications. Salt production in Japan has been for many years far from adequate to supply the domestic demand, especially as a consequence of the rapid

expansion of the alkali industry. Total consumption in prewar years exceeded 2,500,000 metric tons per annum for industrial purposes alone. A little more than a third of all needs was of domestic origin. In general, table salt was produced by the domestic industry and industrial salt was imported. Before World War II, in addition to what it obtained from North China, the leased territory of Kwantung and the Changlu fields, Japan imported salt from Aden, Egypt, Turkey, and elsewhere. Japan requires large tonnages of salt not only for its chemical industries but also for curing fish.

China—The salt industry in China is under Government control and, as there are 400,000,000 consumers, salt plays an important role in the political and economic life of the people. Sources of supply are diverse and widespread. Solar salt works extend along the coast from Korea south to Indo-China and all coastal provinces produce, but Lianning, Kiangsu, Shantung, and Hopeh are the largest producers. Boiling sometimes is resorted to in the final stages of production. Production itself is under private management, the Government function being supervisory. More than 75 pct of China's total salt output comes from sea water.

In the inland areas, salt is produced from brine wells, salt lakes and "salt earth." In the southwestern region, where red beds are present, wells are drilled and mines are periodically flooded. In Yunnan and Szechuan, considerable salt is produced from natural salt brine in wells. In the northwest, salt lakes provide a supply of salt for local consumption. A small supply of impure salt is found along Huangho in Honan, where so-called "salt earth" occurs; the product gathered contains 62 to 86 pct sodium chloride.

The natural salt-brine industry in Szechuan and Yunnan has been developed into a good-sized industry and, by means of crude implements, wells 1000 meters deep have been drilled. All salt is obtained by artificial evaporation with solid fuel or gas. Wells are drilled in red beds in which thin beds of rock salt and disseminated salt are found.

Lake salt is produced mainly in Tsinghai, Kansu, Sinkiang, Suiyuan, and Shansi. Salt mining in lakes is not pursued by professional miners and production is confined to the winter season, when the lake water subsides. The salt is purified by recrystallization. Honan is the only province in which salt earth is produced. The work is intermittent and the quality of the salt is poor. Rock-salt mining is prosperous in Hupeh, Hunan, Sikang, and western Yunnan.⁹

Syria and Lebanon—Syria and Lebanon have numerous salt lakes and an estimated 10,000 metric tons yearly is produced but most of the domestic requirements are met by imports. It would be possible to increase greatly the output from the salt lake at Jebbul, which is quite dry in summer, as the lake covers 240 square miles. In the Middle East,

prior to the war, production was about one million metric tons. The salt is mostly produced by evaporating sea water from the Mediterranean or Red Seas and the salt industry is a Government monopoly.

Turkey—During World War II, Turkey ceased to export salt but resumed its export in 1946. The sources include sea salt, at Camalti, which contributes about 75 pct to the total output; lake operations around the Salt Lake (Tuz Golu), rock-salt mines, and salt springs. The 62 plants, most of them small, produce about 250,000 metric tons annually. The salt industry is a Government monopoly and makes an important contribution to the Government revenue.

Aden—Aden ranks as a leading salt producer. Solar salt is the product, and nearly 210,000 metric tons was produced in 1944.

Iran—In Iran, some rock salt is mined on coastal islands, Quishm and Hormuz, and large deposits are found in other parts of the country. Current production, which is not available, does not meet the domestic need and several thousand tons is imported yearly.

Iraq—In Iraq, salt is produced for local consumption from salt lakes at Buara and near Mosul. Other sources are brine springs. Output has increased nearly three times compared with the late '30s.

Borneo—In Borneo, the industry, centered on the west coast, is making excellent progress, and bids fair to satisfy all the domestic need; and the Government is lending a helping hand, as in tax exemptions, enforcing official salt prices and the granting of subsidies.

Ceylon—The salt industry in Ceylon is a Government monopoly. At present production is not adequate for domestic needs, but the Salt Department is striving to increase it, not only for self-sufficiency but to have a surplus for export.

Miscellaneous—In the Netherlands Indies, salt is a Government monopoly. In Burma, all the salt is produced from sea water, salt springs and saline soils. Production in a recent year was 50,000 metric tons and double this quantity is imported, chiefly from Aden. India's production in recent years has been approximately 2,000,000 tons of salt, a large part of which is solar. There are, however, very important deposits of rock salt in the country.

Africa

Egypt—In Egypt, salt is obtained by solar evaporation at Alexandria and Port Said. A concessionaire operates at each place under Government control. Normally, the combined production of the two operations meet all local needs (65,000 metric tons annually) and provide a large exportable surplus (280,000 metric tons yearly).

French Morocco—A large deposit of salt was uncovered recently near Guercif, French Morocco. It is being developed and is expected to

be producing 1500 tons of salt per month by the end of 1947, a distinct aid to making French Morocco self-sufficient in this commodity.

Kenya—Salt is produced in Kenya by solar evaporation at the Magadi Soda Co., Ltd., and is consumed rather locally. Recent output is about 17,000 to 18,000 tons yearly. Salt is more or less of a byproduct of the soda ash industry at Lake Magadi and is obtained from the material dredged out of the lake.

Southwest Africa—In Southwest Africa, salt comes from rock-salt deposits and from solar evaporation in salt ponds near Swakopmund. Most of the product is consumed locally. Six concerns produce 3000 to 3500 tons quarterly.

Eritrea—Production of salt in Eritrea is by solar evaporation of sea water. Most of it is exported to India and Ethiopia.

Ethiopia—Although salt is produced in Ethiopia, more than half the country's requirements is met by imports from adjacent countries, where it is produced mainly by solar evaporation of sea water. The largest deposit in Ethiopia is in the Danakil depression, a vast sunken zone that reaches 392 ft below sea level and covers 3000 square miles in areal extent. It is estimated that of this area, about 460 square miles are covered by salt, with an estimated reserve of more than one billion tons. The salt, accompanied by gypsum, was formed by the evaporation of the water of the closed basin that was formed by the elevation of the so-called "Danakil Alps," which are between the depression and the Red Sea.

Exploitation is by crude hand methods and production is thought to average about 10,000 tons yearly. The total consumption of Ethiopia is said to be about 28,000 tons yearly. The construction of a truck road from the salt plain of Danakil to the plateau of Tigre Province is needed to replace camel transportation, thus making a larger and cheaper supply available.

Other occurrences of salt in Ethiopia are the saline lakes, Magado and El Sod, near Mega in southern Ethiopia, which occur in the craters of extinct volcanoes. They are exploited on a small scale locally. The brine contains a mixture of salt and sodium carbonate and there is the possibility that these brines might offer a source of soda ash.¹⁴

French Somaliland, Algeria—In French Somaliland and Algeria, and what was formerly Italian East Africa, salt is produced by solar evaporation of sea water.

Tanganyika—In Tanganyika, salt comes from salt springs, in which the Government is a shareholder, and from salt-encrusted dry lakes—for instance, Lake Natron—along the Kenya border.

Union of South Africa—Salt comes from inland salt pans or depressions in the Union of South Africa, in which the salt is yielded naturally

through solar evaporation. The crude solar product is likely to be contaminated by dust and the quality is inferior to the imported European product. If purchasers were satisfied with this type of salt, the Union would be self-sufficient.

POLITICAL AND COMMERCIAL CONTROL

There is no such thing as control of the salt industry, in any sense of the word. Generally speaking, each country is able to take care of its own pressing needs. There is, however, because of special conditions, some commerce in salt and, under the fairly normal conditions that obtained prior to World War II, salt in commerce was a considerable item in specific cases. Cuba imports 20 pct of her salt requirements, mostly of the finer grades for table use. Japan, before the last war, leaned heavily on imported salt for use in her basic alkali industry, the salt coming chiefly from the near-by Asiatic mainland, from the Italian African coast countries, Ceylon and Turkey. Brazil has had to import some salt from Argentina, not because of limited resources, but rather from lack of production facilities.

Even the United States, with all its vast production facilities, imports some tonnage, chiefly from Canada and the West Indies, but the quantities, amounting to only a fraction of 1 pct, compared with its domestic output, are entirely negligible. This imported salt comes to Atlantic coastal ports for use in the fisheries. Exports of salt from this country are considerable and for the most part go to Canada, Newfoundland, Labrador, Mexico, and Cuba; i.e., to the neighboring lands. Total exports from the United States, however, do not amount to much more than 1 or 2 pct of the total output. Exports of salt in recent years have been:

YEAR	SHORT TONS	YEAR	SHORT TONS
1941	123,195	1945	190,524
1942	118,424	1946	223,426
1943	145,803	1947	188,307
1944	198,368		

The Tariff Act that became effective in the United States on June 18, 1930, provides that sodium chloride, or salt in bags, sacks, barrels, or other packages shall be dutiable at 11¢ per 100 lb; and in bulk, at 7¢ per 100 lb. The following special provisions relate to salt:

Imported Salt for Curing Fish—Imported salt in bond may be used in curing fish taken by vessels licensed to engage in the fisheries, and in curing fish on the shore of the navigable waters of the United States, whether such fish are taken by licensed or unlicensed vessels, and upon proof that the salt has been used for either of such purposes, the duties on the same shall be remitted.

Exportation of Meats Cured with Imported Salt—Upon the exportation of meats, whether packed or smoked, which have been cured in the United States with imported salt, there shall be refunded, upon satisfactory proof that such meats have been cured with imported salt, the duties paid on the salt so used in curing such exported meats in amounts not less than \$100.

PRODUCTION AND CONSUMPTION

The history of production and consumption of salt in the United States goes back to its settlement. This follows from its use in the preparation and preservation of food. At first, it was boiled from sea water and the "pioneer village" exhibition at Salem, Massachusetts, established some years ago, is a concrete illustration of its crude beginnings. From such simple beginnings in the early colonial period, the uses of salt have expanded along many lines until the domestic chemical industry alone now consumes about half the total domestic output.

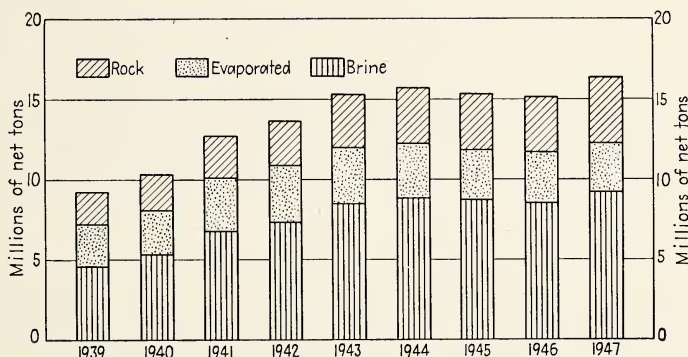


FIG 1—TRENDS IN QUANTITY OF ROCK SALT, EVAPORATED SALT, AND BRINE (IN TERMS OF SALT CONTENT) SOLD OR USED BY PRODUCERS IN THE UNITED STATES, 1939–1947. Minerals Yearbook, U. S. Bureau of Mines.

In Europe, normal conditions would be about the same as in the United States. In the rest of the world, excepting Canada, Australia and Japan, requirements for salt have not kept pace with those either in the United States or in Europe but human consumption has advanced proportionally to increase in population.

In the location of salt-producing plants, the first essential is a plentiful supply of raw material from which to make saturated brine. A good market close at hand is also necessary. Other favorable factors are water for dissolving the rock salt and for plant and cooking purposes. Other important factors are competing railroads, water transportation if possible, cheap fuel, and a good labor supply. The manufacture of coproducts, as bromine or bromine chemicals, calcium chloride, magnesium its alloys and/or compounds, do not appear to be essential to success.

The marketed production of salt in the United States is shown in Table 4. The values are f.o.b. plant and do not include cost of cooperage or containers. The curves of Fig 1, which is for the latest 9-year period, show rapid increase to 1944 with a slight downward tendency in 1945 and 1946, then a recovery in 1947.

TABLE 4—*Production and Value of Salt in the United States*^a

SHORT TONS

Year	Evapo- rated	In Brine	Rock Salt Mined	Total	Total Value	Average per Ton
1935-1939 avg. . .	2,507,374	4,205,587	1,947,254	8,660,215	\$23,405,612	\$2.70
1941.	3,330,106	6,771,436	2,619,087	12,720,629	33,620,376	2.64
1942.	3,517,832	7,373,165	2,802,287	13,693,284	38,144,234	2.79
1943.	3,476,501	8,478,513	3,259,138	15,214,152	41,529,688	2.73
1944.	3,448,578	8,820,355	3,448,238	15,717,171	43,715,492	2.78
1945.	3,182,570	8,705,831	3,505,740	15,394,141	43,914,406	2.85
1946.	3,249,457	8,470,680	3,412,008	15,132,145	44,912,586	2.97
1947.	3,158,718	9,925,303	3,754,353	16,138,374	52,276,180	3.24

^a From Minerals Yearbooks, U. S. Bureau of Mines.

By evaporated salt is meant that produced in single and multiple-effect vacuum pans, grainers, open pans, or ponds or lagoons exposed to the sun's rays. So-called brine salt is converted directly to alkali, hydrochloric acid, metallic sodium, or chlorine, and does not appear in the trade as such.

The leading position in the salt industry is occupied by Michigan, New York and Ohio being in rather distant second and third places. The two southern states, Louisiana and Texas, are, respectively, fourth and fifth in order of output. In all, 73 plants controlled by 50 concerns operated in 1946 compared with 72 plants (58 companies) in 1936. There is a tendency for the number of plants to decrease from the maximum attained during World War II; that is, 86 in 1942.

Production capacity has usually exceeded demand but in recent years—for example, 1945—most of the saltworks ran at or near maximum capacity.⁷

WORLD PRODUCTION

Considerable doubt is cast on statistics of world salt output in recent years, especially since the beginning of World War II, because unsettled conditions led to incomplete and unavailable data. Prior to the war, the output of the United States ranged around 30 pct of world output, but in tables prepared by the writer the proportion has steadily increased to 60 pct in 1944, owing, it is believed, to incomplete returns from foreign lands. There are, for example, no data from Japan in recent years. Without much doubt, the United States maintains first

place among the nations in salt output, with Germany second and Great Britain third. India and China are listed among the large producers because of their populations. In the two last-named countries, as in most of the rest of the world, the tonnages used in chemical manufactures are comparatively small.

Perhaps 25,000,000 metric tons—certainly not more than 30,000,000 metric tons—may be considered a close approximation to present world output.

PROSPECTING, EXPLORATION AND MINING

Salt, a highly soluble mineral, does not appear at the surface except in arid regions. In the West, for example, outcrop areas of salt occur in Utah, Nevada, New Mexico, California, and possibly in other states. In areas of abundant rainfall, salt usually is buried so deeply below the surface that it can be found only by drilling. The history of the discovery of salt in most places shows that it has been found incidentally; most often, perhaps, in the endeavor to find other substances, chiefly oil, gas, and water. This has generally been true among the salt domes of the Gulf Coast states, but it is not always so, however; the presence of brine springs in the vicinity, or even in remote locations but with an indicated geological relationship, has led to the discovery of strategically located rock-salt deposits. A conspicuous example is the brine springs near Syracuse, New York, which led, as a result of geologic reasoning, to the discovery of rock salt in Onondaga Creek Valley, 18 miles to the south of that city.

Salt is mined to some extent like the bulk of other minerals, but by far the greatest part of it is produced by dissolving it underground. The more or less completely saturated brine is lifted to the surface and the succeeding steps leading to the finished product may be considered a metallurgical process of refinement or a chemical process—less appropriately, a manufacturing one, though it is commonly referred to by that term.

Ordinary water at air temperature is allowed to enter the well by gravity and the brine formed is lifted to the surface (a type of hydraulic mining), settled, purified, and evaporated. It is obvious that the weight of the water column will lift the brine column a certain distance, depending on their relative specific gravities; 100 parts of water at ordinary temperatures dissolve a little more than 35 parts of salt by weight, giving a solution that contains about 26.5 pct of salt, having a specific gravity of about 1.2, therefore a column of water of certain height will lift a column of saturated brine to $\frac{5}{6}$ of that height. The brine is lifted the remaining distance (the actually applied lift) by compressed air—an airlift, as it is usually called. Under certain circumstances, where it is feasible, direct pressure may be used to lift

the brine the required distance, and hydrostatic pressure is the cheaper means. Pumps also are employed.

An ingenious method of dissolving rock salt in place is now practiced to some extent. It is sometimes referred to as the Trump method, from the name of its inventor.²⁷ In this method, a horizontal layer is dissolved at the base of the salt bed. Mud and other insoluble impurities fall to the bottom of the cavity, or to the top of the underlying barren formation. Thus impurities are once and forever out of the way. Thus the disadvantages of a conical cavity with a succession of roof caves, rupture of tubes, casings, and stoppage of production while cleaning out is in progress, are largely avoided.

The solvent water is kept from touching the saline roof by means of an air cushion, provided by entrained air carried into the well by the flow of feed water. A constant level of the solvent is maintained by providing an escape of the surplus air not dissolved in the brine. The height of the dissolving water thus is optional.

In operating the Trump plan, the dissolving water is at first kept at about 4 ft above the base of the well, which therefore represents the thickness or vertical dimension of the first slice or undercut. When this is completed to the diameter desired, the air cushion may be raised in 10 or 20-ft stages, thus bringing the water solvent into contact with the extensive saline surface above the first undercut. Solution of the salt proceeds until a cavity of 300 to 500 ft or more in diameter is formed. A cavity of this size probably will support itself. Even though there might be some caving from the roof, it would not be particularly disadvantageous unless it occurred too near the metal tubing. The great advantage of this method where the original roof of the salt bed is soft is obvious.

PREPARATION FOR MARKET

The different kinds of salt marketed are: vacuum-pan, grainer or open-pan, solar and rock salt. Pressed blocks of salt may be made from both evaporated and rock salt. The first three types mentioned come under the general classification of evaporated salt.

The brine coming from the wells contains soluble impurities, chiefly hydrogen sulphide gas, iron compounds probably as carbonate, and calcium and magnesium salts. For the purest grades of salt used in the food industries and for special purposes, these are largely removed by chemical means. The brine may be aerated, treated with lime or lime and soda ash, caustic soda and soda ash, and possibly alum, and allowed to settle a few days. Some manufacturers chlorinate the raw brine for the removal of sulphides and oxidation of the iron. The brine is then aerated to remove the excess of chlorine and the chemicals added. In

the manufacture of vacuum-pan or grainer salt for the most exacting trade, the brine may be purified by the lime-soda-ash process, and for this trade, largely the dairy, some manufacturers consider the cubical grained or granulated salt as good as the flake grainer salt.

The addition of such chemicals as lime and soda ash should be under close chemical supervision. Chemical dosage and control may be based on the pH value, or, preferably, on actual chemical analysis or alkalinity of the purified product. When purification takes place in the open, the brine surface always gathers some dust or fly-ash and this must be avoided as far as possible.

Ingenuous chemical methods based on sound principles have been suggested to prevent formation of scale in vacuum-pan operations, such as taking advantage of the calcium chloride naturally present in the brine. In the manufacture of vacuum-pan salt, trisodium phosphate is sometimes added to the brine either in the pan or before it goes into the pan. Doubtless other chemical devices are used, which have not come to the writer's attention. The next step in the preparation for market is the actual crystallization of the salt from the brine by the methods already stated.

The vacuum pans used in making granulated salt are generally of the vertical type. They consist of long vertical tubes, the ends of which are expanded into two plates, forming diaphragms across a cylindrical shell near the ends, the space between being the steam chest. There may be one or more in series, and they are referred to as single "effects," double or triple "effects," depending on their number. Those used in the evaporation process generally have deep cone bottoms. Usually they work with low steam pressure (5 lb) and are run on a vacuum of 28 in. Usually such evaporators have large central downtakes and are fitted with special propellers for better circulation of brine.

The salt is recovered in closed filters either periodically or by a continuous vacuum process, or by bucket elevators. Without proper pretreatment of the brine, scales form and evaporation is retarded. Scaling, unless preventive chemicals are used, must be performed daily by mechanical means. Some brines foam and a large vapor space is required. Evaporators generally are built with cast-iron shells and copper or brass tubes, but iron tubes also are used. Very large units are the order of the day, even reaching a capacity of 1000 tons daily.

Vacuum-pan salt is made up of fine, lustrous grains, and by virtue of its fineness and purity is particularly suitable for the table, for canning foods, and in the manufacture of patented prepared flours, which have become so popular in recent years. It is better known to the trade as granulated salt. Each producer has his own classification but in general table salt is about 30-mesh. Still finer grades, say through 30

and on 50-mesh screen, is commonly referred to as salt flour and is used in the patented baking flours. The grades coarser than table salt are largely consumed in the canning industry. Granulated salt may also go into the different dairy products.

To render certain grades of table salt moistureproof, so as to make them run as freely as possible, a small quantity, usually not more than 1 pct of some nonhygroscopic substance like magnesium or calcium carbonate or phosphate, is used to coat the grains. The product is the familiar "shaker" or free-running salt. Some salt is now mixed with a minute quantity of potassium iodide to make iodized table salt. The table grades for household use are packed and shipped in the familiar pasteboard cartons of circular or rectangular section, or in small cotton sacks, filled and sewed by automatic machines.

Grainer salt, a coarser grained product than vacuum-pan salt, is made in elongated shallow pans, built of steel or concrete and heated by steam coils. The salt formed is removed by mechanical scrapers moving back and forth along the bottoms of the pans. They work with low-pressure steam. The texture of the salt prepared by the slow evaporation in grainers is quite different from the granular vacuum-pan product and from rock salt. Grainer salt is flaky or has thin, flat grains. After leaving the grainers, it may be centrifuged until it contains about 6 pct moisture, then artificially dried in kilns. It is desirable to have it rather coarse, grading from 10 to 40-mesh. The less it is handled, the better, for handling reduces the proportion of coarse salt.

In making butter, flake grainer salt of 10 to 20-mesh size is commonly used; and in cheesemaking 20 to 40 or even 60-mesh size is often used. The finer grades do not always find a ready market and are disposed of as advantageously as possible. Some grainer salt may be shipped unsized.

Solar salt from sea water is made in certain parts of California, notably along the shores of San Francisco, Monterey, and San Diego Bays and at Long Beach. It is also made at Saltair, along the shore of Great Salt Lake, Utah. More than 95 pct of the California output is produced originally in this manner. Intake ponds are flooded from the bays at certain intervals at high tide. From these the salt water is pumped into secondary ponds or basins and gradually transferred from pond to pond as the brine strength increases. The concentrated brine or the crude solar salt is finally treated according to the kind of salt required, or may be sold in the original form for certain purposes. Solar evaporated salt is made much more extensively in southern Europe, in Asia, Africa, Oceania, and South America than in the United States.

Rock salt is not purified but is prepared for market by crushing and screening. The four commercial sizes of rock salt from the Retsof mine, New York, are No. 2, No. 1, Coarse C and Fine C, sized as follows:

Size	Through	Retained on
No. 2	0.525-in.	3-mesh
No. 1	0.371-in.	4-mesh
C.C.	3-mesh	8-mesh
F.C.	8-mesh	none

At the plant of the Jefferson Island Salt Co., Louisiana, all salt above $\frac{5}{8}$ to $1\frac{1}{4}$ -in. is called No. 3 salt and is billed for bulk loading, sacking or milling. The oversize above $1\frac{1}{4}$ -in. is scalped off and put in the brine. The resultant $\frac{5}{8}$ to 9-in. is then fed to a battery of four Hummer screens, where No. 2 salt, $\frac{3}{8}$ to $\frac{5}{8}$ -in., is discharged on a belt and conveyed to the bin. No. 4 salt, $\frac{3}{8}$ to $2\frac{1}{2}$ -in., is also taken out by this battery of screens. The resultant product is then fed to a second battery of screens on the floor below where No. 1 salt, $2\frac{1}{2}$ to 4-in., and C salt, 6 to 10-in. mesh, are screened and binned.

Practically the same process is used in mines all over the country. The grades of salt from the Detroit mine of the International Salt Co. are about the same as at Retsof, but in Louisiana the mines produce several grades, ranging from the coarsest, which is about $\frac{3}{4}$ -in. to 18-mesh, to the finest, which is sold as table salt.^{10,20}

During the past four decades or so, pressed blocks of salt have come into the market as a substitute for the large lumps of rock salt used in field and stable for salting cattle. They weigh about 50 to 60 lb and are made in hydraulic presses under great pressure, sometimes as high as 20,000 psi. Fine grades of evaporated or rock salt may be used in their manufacture, but the salt should be dry. Imperfect blocks are sawed into smaller blocks or bricks. Blocks are made sometimes with a small admixture of sulphur, supposed by some to give them medicinal value. Some concerns produce a mixture known as "smoke salt," for curing meat at home, which is said to contain sugar, seasoning, a small quantity of pyroligneous acid and probably niter.

MARKETING

The marketing of salt is a large subject and a special report thereon has been issued by the U. S. Bureau of Mines.⁶ The office of the National Recovery Administration, Division of Review, published an article by Irwin S. Moise and George B. Haddock.¹³

This study is largely devoted to marketing practices in the salt industry. It covers 94 pages and describes in some detail the background of the industry, under which there are described: (1) relative production costs, (2) the Salt Producers Association, (3) selling practices. Under the last mentioned heading there is included a discussion of: (a) sales made on delivered basis, (b) marketing areas and freight equalization, (c) open price system and channels of distribution.

The proposed code of fair competition for the salt-producing indus-

try is mentioned and there is an elaborate discussion (pp. 137-142) on how the code program developed to meet the more basic problems of the industry; e.g. (1) how to decrease bulk sales and increase package sales, on which there is a greater profit, and (2) how to eliminate or subjugate price competition and the other obstacles to price uniformity.

Another part of this report covers trade practices affecting channels of distribution, which are listed herein under the heading of "Prices."

The report closes with a summary and analysis of the problems confronting the salt industry, the methods selected by the industry to solve its problems, and the results of such methods.

A Bureau of Mines report by Miss F. E. Harris⁶ considers the following topics, specifically appropriate to the subject of marketing: (1) organization of the domestic industry, (2) market areas, (3) sales channels and mechanics of marketing, (4) packing, (5) prices, (6) discounts, (7) coastal markets, and (8) transportation and storage.

The reader is referred to these two publications for the voluminous detail on this subject of marketing salt, as the scope of this paper prevents any elaborate descriptions on the subject.

TESTS AND SPECIFICATIONS

There has been no change since 1937 in the definition by the U. S. Department of Agriculture of table and dairy salt. The definition then, as given in the first edition of this book, was: "Table and dairy salt is fine-grained crystalline salt, containing, on a water-free basis, not more than 1.4 pct of calcium sulphate (CaSO_4), not more than 0.5 pct of calcium and magnesium chlorides (CaCl_2 and MgCl_2) nor more than 0.1 pct of matters insoluble in water. Pending further statement, no exception will be taken by the Food and Drug Administration to table salt that meets the requirements of the standard except that it contains anhydrous calcium sulphate (anhydrite) in excess of 0.1 pct, provided that the total calcium sulphate content does not exceed 1.4 pct."

USES

The uses of salt, classified and tabulated statistically by the U. S. Bureau of Mines, are given in the Minerals Yearbooks, and for accuracy and completeness, no published figures can approach them. For greater convenience, these figures for the past six years have been rearranged and presented here in Table 5. For the greater detail, the reader should consult the original compilations.²⁹

By far the largest consumption of salt goes into the preparation of soda ash, wherein the salt is used in the form of brine. The second largest use is in the manufacture of chlorine, bleaches, chlorates, and so

TABLE 5—*Salt Sold or Used by Producers in the United States, 1942-1946, Classified According to Uses^a*
SHORT TONS

Use	1942	1943	1944	1945	1946	1947
Soda ash.....	6,670,859	7,157,644	7,340,102	7,087,227	6,957,592	7,467,138
Chlorine, bleaches, chlorates, etc.....	2,202,883	2,656,293	2,865,349	2,532,975	2,386,854	2,741,812
Misc. chemicals.....	900,112	1,111,443	1,069,086	1,119,128	1,153,944	1,196,716
Dyes, organic chemicals						
Soap precipitant						
Other chemicals						
Textile processing						
Hides and leather						
Food industries.....	1,278,673	1,413,325	1,401,572	1,374,432	1,340,762	1,376,096
Meat packing						
Fish curing						
Butter, cheese and other dairy products						
Canning and preserving						
Other food processing						
Refrigeration.....	185,546	210,993	235,928	281,353	269,677	236,972
Livestock.....	803,225	858,405	764,974	732,746	791,881	733,856
Highways, railroads, dust and ice control..	211,165	296,043	228,203	317,805	320,124	473,704
Table and other household.....	684,784	665,525	602,615	682,281	707,850	652,058
Water treatment.....	375,190	374,478	349,451	376,386	425,445	452,142
Agriculture.....	98,668	62,582	64,778	56,766	31,872	23,983
Metallurgy.....	65,337	74,893	66,116	57,922	48,969	87,121
Other uses.....	216,842	332,526	728,917	775,120	697,175	706,776
Totals.....	13,693,284	15,214,150	15,717,091	15,394,141	15,132,145	16,138,374

^a Data from Minerals Yearbooks, U. S. Bureau of Mines.

forth, where it is used principally in the form of brine but also in large quantity in the form of rock and evaporated salt. Next, or third in tonnage, comes the aggregated food industries, as meat packing, canning and preserving, the dairy industries, fish curing, and the manifold other food-processing industries. Next in order of importance appear the miscellaneous chemical uses, which include, in order of importance, miscellaneous "other" chemical, hides and leather, textile processing, dyes and organic chemicals, and soap precipitant.

These four main uses of salt are followed by its use in livestock feedings, table and other household use, water treatment, dust and ice

control on highways and railroads, refrigeration, agriculture, metallurgy, and "others."

As intimated above, on account of the difficulty of apportioning exactly the tonnages of salt used in the different chemical and food industries, it has been thought advisable to make these two grand divisions. Doubtless part of the salt consumed in the manufacture of organic chemicals could be just as well included in "other" chemicals, or vice versa; also part of the salt included under "canning and preserving" and "other food processing" could just as well be included under "meat packing," or vice versa. We know that some salt used for chlorine has been included under "dyes and organic chemicals."

The accompanying illustration (Fig 2) furnished through the courtesy of The International Salt Co., of Scranton, Pennsylvania, gives some additional ideas on the ramified uses of salt.

For a complete statement on uses of salt with illustrations, the reader is referred to an article by C. D. Looker, of the International Salt Co.¹⁰ The newer uses of salt are of great interest and importance. These include the important organic chlorides, the chlorine in which goes back to salt as the starting point. Synthetic rubber, DDT, the manufacture of metallic magnesium, and the use of salt as a fertilizer are among the newer applications; also the expanding uses of metallic sodium, hydrochloric acid, caustic soda, and so forth, are increasing the market for salt. Whether it be used as such or in the form of its numerous derivatives, salt must be listed among the most important minerals; in one or more ways, it enters directly or indirectly into the manufacture or preparation of a large proportion of the common commodities that are met with in life's daily walk.

PRICES

No adequate picture of prices can be given in this chapter. The subject is too involved. Moise and Haddock¹³ devote a section of their report to trade practices affecting channels of distribution, wherein there are discussed: (1) customer classification, (2) resale price maintenance, (3) price differentials, (4) quantity discounts, (5) discounts other than quantity or trade, (6) consignments, (7) brokerage, (8) restrictions on sales to certain classes of outlets, (9) restrictions on size or manner of making shipments, (10) price discriminations. The diversity of topics alone will indicate how intricate the subject is to those outside the trade.

The following statement by F. E. Harris⁶ is of interest:

"Salt is sold on a delivered basis, and prices in various parts of the United States are far from uniform. Price lists of salt are published from time to time by members of the Salt Producers Association and are furnished to its head office for filing or for the information of other members. The lists pertain to past transactions, as it is not the policy of

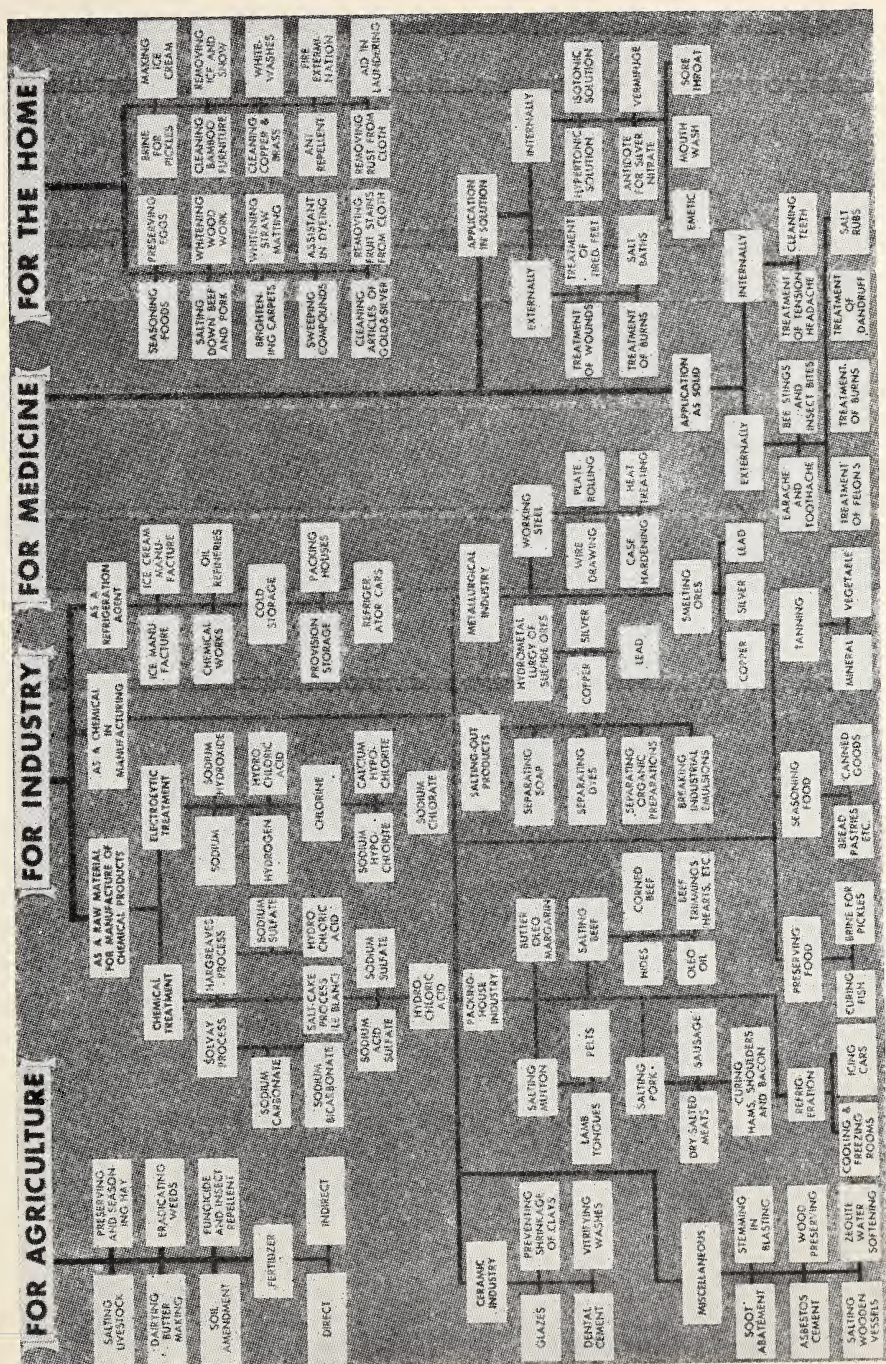


FIG 2--RAMIFIED USES OF SALT.
By courtesy of International Salt Company.

the association to attempt to reach any agreement with respect to future prices. Moreover, the printed price lists constitute the basic prices and, in that condition, do not reveal what the average consumer pays, even in a given market area, for they do not include transportation costs or sundry other items, such as various discounts. The basic prices applying to a natural marketing area are fairly uniform with regard to the same or comparable grades of salt, but the schedules may vary between areas."

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CHAPTER 41

SAND AND GRAVEL*

BY BROR NORDBERG†

SAND and gravel are unconsolidated granular materials resulting from the natural disintegration of rocks. The two materials nearly always occur together, variably proportioned in widely available deposits. A commercial sand comprises the fine granular material, usually less than $\frac{1}{4}$ in. in diameter (ASTM Designation C58-28), and gravel consists of the coarse, granular material larger than sand (ASTM Designation C125-46T). Gravel falls within the range of $\frac{1}{4}$ in. and a top size usually of $3\frac{1}{2}$ in.

Chemical definition is impossible. Sand and gravel are always of secondary origin. They were formed from various massive rocks through the action of chemical and mechanical forces; then transported, abraded, washed, sorted, and classified by streams, glaciers, waves, or winds, to be redeposited in beds as they are found.

Chief disintegrating forces in the reduction of rocks into granular particles were frost, rain, the dissolving action of acid and alkaline ground waters, the mechanical action of streams and waves, and the action of glaciers.

Method of formation and deposition have imparted physical properties to sands and gravels that largely determine the commercial value of the materials for particular use and influence the manner of exploitation. In the early days of the commercial industry, purchasing specifications were relatively lenient but in the past decade much more rigid quality requirements have had to be met for acceptance by all classes of purchasers. The trend to further severity in requirements is a challenge to the industry that commands full knowledge of the nature of raw materials at hand and skillful application of processing into commercial products.

Mechanical strength, the ability to resist disintegration, chemical

* This chapter is concerned with gravel and sand as used for construction purposes, as aggregates, railroad ballast, and so forth. Sand for industrial use (glass manufacture, foundries) is considered in the chapter on Special Sands. The author has drawn from the chapter on Sand and Gravel by J. R. Thoenen in the 1937 edition of this book, for basic information and discussion of methods that have continued to be accepted practice.

† Editor, *Rock Products*, Chicago, Illinois.

stability, cleanliness, particle shape and grading are the principal properties sought in commercial sand and gravel.

Color of sand and gravel varies from the white of pure quartz through various shades of brown to the black sands consisting of heavy iron-bearing, nonsiliceous minerals such as magnetite and rutile. Unit weight for loose, dry sand and for gravel ranges from 90 to 110 lb per cubic foot.

CLASSIFICATION OF DEPOSITS

Commercial sand and gravel deposits are classified in four main categories, according to origin, as follows: (1) fluvial; (2) glacial; (3) marine and lake; and (4) residual. Aeolian formations are of relatively minor importance.

Fluvial deposits are those resulting from the transportation of sand and gravel by streams. Such deposits exhibit stratification and often show rough size gradation. The beds vary in thickness and sometimes are interspersed with lenses of clay or fine sand. Particles usually are poorly sorted and the degree of angularity or roundness varies with their hardness and the distance transported. Fine sands preponderate where there are meanders in the transporting stream. Rivers are constantly building, reworking, and tearing down bars within their channels and it is not uncommon for worked-out outwash deposits to be replenished with sand and fine gravel in regular cycles during periods of high water.

Other typical fluvial deposits are those laid down in wide flood plains by receding streams, those formed in deltas, terraces left behind as old streams flowing in wide valleys cut their way to lower levels, and materials dropped on broad, flat plains by swift mountain streams as they fan out from narrow canyons or gorges.

Much of the commercial production of sand and gravel is from fluvial deposits, many of which are deficient in the fines that are required by present-day grading specifications for concrete aggregates.

Glacial deposits occur in large areas that were covered by the great ice sheets and in adjacent areas. Glaciers brought down tremendous quantities of boulders to form gravel and sand over north central and northeastern United States, southern Canada and, incidentally, the northern half of Europe. Glacial drift is a mixture of hard and soft rock particles of whatever varieties existed in the affected area and has the least sorting of all deposits.

Marine and lake deposits exhibit the best sorting, with coarse and fine particles often well segregated. Gravel sizes are usually well rounded and smooth, and sand sizes range from angular to well rounded particles. They are essentially of hard, tough materials.

Residual deposits are found overlying the parent rock and are unstratified mixtures of pebbles, boulders, sand and clay occurring in all

manner of proportions. They often contain much soft material, resulting from prolonged weathering, and frequently are so intermixed with clay as to prohibit commercial exploitation.

Residual sands and gravels and glacial drift in many deposits contain much feldspar and limestone among their softer constituents. They vary markedly in the hardness of individual particles. Particles are angular or sharp-edged whereas transported sands and gravels are of subangular to well rounded particles that approach quartz in hardness.

In a few isolated cases, glacial gravel is sufficiently high in limestone particles to have commercial value as agricultural liming material and is pulverized and marketed as a product in excess of 80 pct calcium carbonate equivalent in competition with agricultural limestone. A leading supplier is furnishing gravel for use as flux in the manufacture of steel.

SUPPLY OF SAND AND GRAVEL AND SUBSTITUTES

Sand and gravel are available in nearly every county of the United States and commercial production is largely governed by local demand. They are worth little in the ground and their market value, which averages less than their average unit cost of transportation (for the nation), derives from the cost of preparation. Equipment investment is high, competition is keen, and operations range from very simple roadside pits to plants having capacities as high as 1000 tons per hour.

Fine aggregate manufactured by special processes to impart desired particle shapes has been introduced in commercial crushed-stone plants to a limited extent in competition with natural sands where suitable natural sand is scarce. Waste fine sizes of stone are sometimes processed to required gradation and, in a few states, is permissible for concrete highway construction. Some specifications require that manufactured sands, when used, be blended with natural sand in approximately equal proportions. A true manufactured sand is made by crushing and pulverizing ledge rock, screening it and grading it by either hydraulic classification or air separation. These products nearly always contain greater percentages of minus 50-mesh and minus 100-mesh particles than are available in competitive natural sand, to meet prevailing requirements for fines in high-specification sands. High percentages of minus 50-mesh and 100-mesh particles are required in manufactured sands to minimize harshness associated with concrete made from angular fine aggregates.

Light-weight aggregates, including prepared, expanded cellular blast-furnace slags, Haydite (burned shale), cinders and, very recently, glassy rocks including pumice, perlite, and obsidian, are finding increasingly wide acceptance for the manufacture of light-weight concrete masonry units and in the construction of structural concrete walls, roofs, and floors where lightness in weight is a factor.

POLITICAL AND COMMERCIAL CONTROL

The sand and gravel industry is a domestic industry and, under normal conditions, production depends heavily on road-building activity.

U. S. Bureau of Mines figures for 1946,¹⁰ a good high-production year, revealed that 2121 commercial operations produced 187,130,000

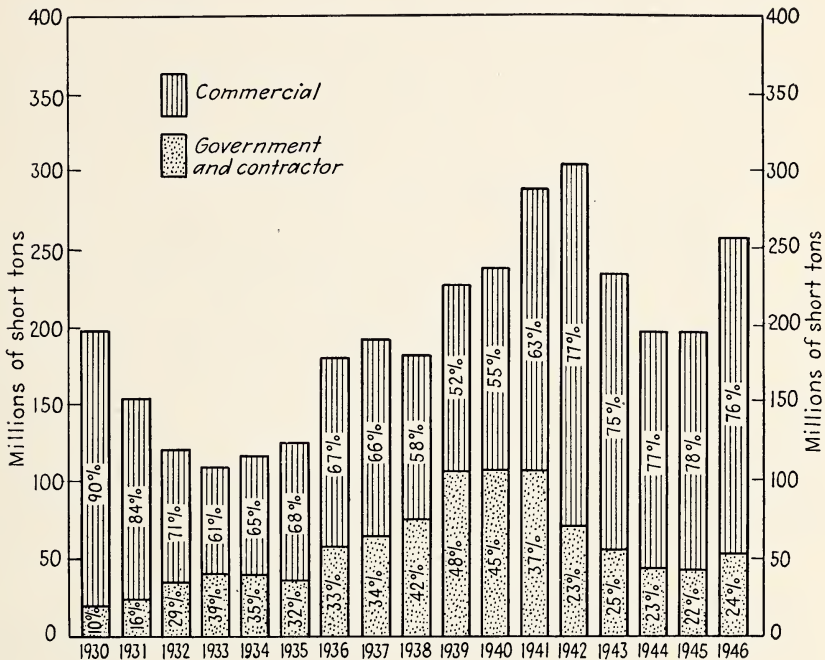


FIG 1—PRODUCTION OF SAND AND GRAVEL.

Data from Minerals Yearbooks, U. S. Bureau of Mines.

short tons of sand and gravel, exclusive of operations by states, counties, municipalities and other government agencies, and not including 4,962,000 tons produced by 133 railroad plants. Total tonnage, including non-commercial production, was 254,131,000 short tons valued at \$171,386,000. Of the total commercial tonnage, 4.0 pct was the output of 39.5 pct of the plants in the less than 25,000 tons per year size classification. Plants in the 50,000 to 300,000 tons size range, numbering 37.3 pct, produced 51 pct of the total tonnage. Average commercial production was 88,200 tons per plant. Of the total commercial tonnage, 51 pct was shipped by truck in 1946, 40 pct by railroad and 9 pct by waterway. An increase of 8.6 pct in the tonnage moved by truck since 1944 and 10.1 pct decrease in rail shipments reflects the railroad-car shortage since World War II, greatly increased freight rates and the stimulus of

increased road maintenance and highway building. Nearly all non-commercial tonnage moves by truck.

California was the largest producer of commercial tonnage in 1946, followed by Illinois, Michigan, Wisconsin, Ohio, New York, Texas, Minnesota, and Pennsylvania, in that order. These nine states, each with

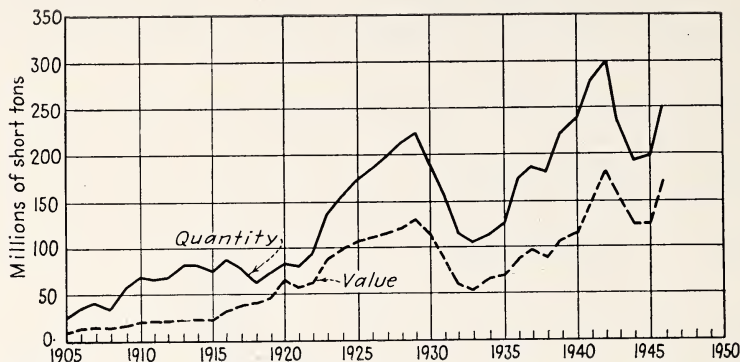


FIG 2—VARIATIONS IN TOTAL PRODUCTION OF SAND AND GRAVEL RELATIVE TO TOTAL VALUE, 1905-1946.

Data from Minerals Yearbooks, U. S. Bureau of Mines.

an output in excess of 10,000,000 tons, accounted for 52 pct of the national tonnage.

Trends in commercial and noncommercial production of sand and gravel for 16 years are shown in Fig 1, and the relation of total annual value to all tonnage from 1905 to 1946 in Fig 2.

PROSPECTING AND EXPLORATION

Prospecting for sand and gravel is to find deposits containing suitable sources of materials that may be economically processed into commercial products. Having discovered a likely deposit for exploitation, the prospector must then determine by test the probable commercial value before taking any steps toward exploitation.

The prospector may set out to search for a deposit as shown by outcroppings and visible deposits under water, through systematic examination of the entire area under consideration. Railroad or highway cuts and deposits known to exist from information derived from excavations for buildings, the sinking of wells or post holes, are examined.

Topographic and geologic information are often relied upon as a guide in finding probable localities by eliminating from consideration areas that have unfavorable topographic or geologic structure. Published reports of the Federal and State Geological Surveys are the fundamental bases on which such a procedure is started.

Careful exploration of a likely deposit is essential to the determina-

tion of its commercial value. Size or extent of a deposit must be ascertained in order to predetermine the size and probable life of plant operations but it is of greater importance that the material be carefully sampled and tested to determine its physical characteristics. Natural size gradation must be considered in its relation to specification requirements and probable market demands.

If controlling specifications require crushed gravel, the availability of sizes amenable to crushing must be known. Modern specifications for gradation of concrete sands that limit within close tolerances the size fractions permissible between five or six pairs of successive test-sieve sizes and specify high percentages of minus 50-mesh particles, with definite minimum percentages finer than 100-mesh, place emphasis on the value of accurate exploration.

Soundness, crushing strength, and the presence of deleterious materials must be determined before the decision is made to process materials from any deposit, and other physical characteristics of relatively minor importance must be considered. Impurities of various sorts can be eliminated or reduced in quantity (see section on Preparation for Market later in the chapter) but there is a limit beyond which processing is neither economical nor practicable. Specifications of recent date (see later section on Specifications) require that plants be operated to improve inferior materials considerably as a condition to acceptance.

The existence of unsound materials (certain shales, cherts, soft particles, and others) and heavy clays difficult of removal must be anticipated. Their presence may prohibit operation or their removal be too costly for economical production.

No two deposits are alike and it is impossible to determine with any assurance of accuracy the nature of the material to be encountered as mining progresses unless through thorough advance exploration.

Relative ratio of gravel sizes to sand and that relation to market demands bear heavily on efficient plant operation. More often than not, there is an excess of sand, and it is not uncommon in some areas to waste back into depleted workings as much sand as is marketable, or possibly more. Deposits under excavation for sand and gravel may have a slight excess of sand, while, in extreme cases, the ratio may be as high as four parts or more of sand to one of gravel. The ideal proportion where usage is principally for concrete construction would be approximately 60 pct gravel, which does occur in a few scattered locations.

An adequate program of exploration requires examination of the material over the entire area under consideration, which means that holes or pits must be opened at sufficient intervals to yield samples that will be representative of the entire deposit. These samples must then be tested to determine whether or not the material is suitable for processing.

When the overlying soil is loose, the gravel deposit can often be out-

lined by use of an iron bar, which, by churning, can be forced through the soil by hand. When the bar strikes gravel, a distinctly metallic sound and sudden difficulty of penetration indicate its presence. Pointed steel pipe may be used for deeper holes, usually up to 15 ft, unless the overburden is thick or very dense. No samples are recoverable by these methods, which are valuable principally for outlining a deposit. Earth augers or ordinary post-hole diggers are sometimes used to determine the thickness of overburden.

Churn drills are employed by many operators, with or without casing, in the exploration of gravel deposits, and fairly accurate information can be obtained from their use. Power-driven churn drills probably are most widely used, since they can be applied successfully to depths of 50 ft or more. They can supply information as to the depth of overburden and the thickness and quality of gravel. The churn drill is applicable for exploration below water level.

Typical practice, when churn-drill holes are used for preliminary exploration in large areas, is to sink holes approximately 400 ft apart in a row to depths of 18 to 20 ft if no gravel is encountered. When gravel is struck, the holes are driven at about 200-ft intervals, to determine the limits of the deposit. The first row is paralleled by others that are 200 to 400 ft apart. All holes are staked and numbered.

The foregoing methods are common procedure for outlining the boundaries of a deposit and for obtaining preliminary samples, but for determining accurately the gradation of material in land deposits, and its quality, test pits are the most reliable and accurate method, as they are more accessible for securing accurate data.

Exploration is meaningless unless samples are representative enough so that test data are accurate, therefore it is necessary that test pits and/or drill holes be systematically placed over the entire area. Practice of some operators is to open up a long face and test all fractions of the material from top to bottom and at regular intervals along the face. The object, by any method, is to obtain a continuous sample from top to bottom of the test pit.

In sampling from test pits, a vertical channel is cut in the wall and the excavated material is caught in sample boxes held against the wall. New sample boxes are substituted at frequent and regular intervals, probably for each 5 ft of depth unless unusual occurrences are encountered. Records are kept for all the samples, indicating the hole number and the limiting depths represented by the sample; also of unusual occurrences such as large boulders, water seams, and changes in bedding. In loose, dry, sand deposits, by nature more homogeneous, it is often sufficient to take a channel sample across the floor of the pit at each vertical foot of depth.

In sampling by churn drill or bailer, or wherever water is encoun-

tered in the hole, accurate samples are obtainable only where the casing can be driven ahead of the drill bit or sand pump. All material, whether coarse or fine, must be saved for each vertical increment cut by the drill, meaning that the material in suspension must be saved. To accomplish this, all material including water should be placed in a box and the fines allowed to settle out before the water is permitted to escape.

Prospect trenching with angledozer has possibilities for quick and economical preliminary exploration of prospects for which there is insufficient information to warrant drilling. Such equipment is cheap to operate on bare or grassy slopes with overburdens in the 5 to 10 ft range of thickness, where the soil can be sidecast and no roadway need be built.

DEVELOPMENT OF DEPOSITS

Information derived from prospecting and exploration largely governs the selection of a plan of operation and the types of equipment to be employed, but other factors outside the realm of technical procedure often influence decisions as to exploitation methods even more importantly. Capital available for plant construction and operation, the available markets and their bearing on desired capacity, are to be considered. Physical character of available materials in a deposit, range of uses for the finished products, mining conditions, scope of required washing and preparation processes, the availability of water, transportation facilities and distances to consuming centers, are factors of which any one, if unfavorable, may rule out an otherwise technically sound property from the point of view of production.

Topographic conditions present problems in planning for development. A bank deposit occurring above the surrounding country demands a plan for operation quite different from that for pit deposits below the ground level. Generally, more than one class of equipment is available for excavation of sand and gravel from very similar deposits.

Size and shape of a deposit will influence the nature and extent of development. Location of the water table and its fluctuations control development procedures for pit deposits.

Generally, where the water table lies just below the ground surfaces, as in Louisiana, excavation by hydraulic dredge pumps is the established procedure, but in thin deposits inability to float a dredge may dictate the use of draglines, cableway slacklines, or other excavating methods.

Three types of dredges, the hydraulic pump dredge, ladder dredge and clamshell dredge, are commonly employed for wet pit operations, in that order of frequency. Nearly always, a pump dredge excavates and delivers material through pipe lines to a land plant for processing. Its limitations are in deposits where large cobble sizes of gravel occur frequently or where the material is somewhat consolidated or agglomer-

ated. Submarine blasting, the use of bank-scarifying equipment and cutters operating just ahead of the suction nozzles, are auxiliary devices sometimes employed under those conditions. The other two classes of dredges nearly always deliver to barges for transfer to a land plant for processing, though, on occasion, the sand and gravel are processed on the dredge and delivered into barges to be towed to distribution centers, or, as partially processed materials, to land plants for rescreening into finer gravel sizes and further classification of sand.

Clamshell dredges are peculiarly suited for underwater deposits containing excessive quantities of debris, and that class of dredge and ladder dredges are adaptable for excavation of material lying at great depth under water. Operators of many ladder dredges claim great flexibility in obtaining the approximate desired proportions of sand and gravel.

A number of plant operators have changed their plans of development as workings extended far from plants, and as unforeseen conditions were confronted. Typically they have converted from hydraulic dredge operation to dragline excavator for handling materials tending toward the conglomerate; or from dragline and power shovel to hydraulic dredge in pit operation, in order to excavate farther down, below the water level, rather than exceed the economical length of haul by motor truck; or from shovel to slackline cableway as subterranean water was encountered.

Hydraulic dredges frequently are operated in relays, as distances exceed the delivery range of a pump. Sometimes two pumps are operated in the line, with synchronized drives, but usual practice is for the discharge of one dredge pipe line to become the feed for a second independent dredge. Variations in the occurrence of sand and gravel, and even in the sizes of gravel, as they are available, sometimes justify operation of two or three dredges at widely scattered points in a single deposit, in order that desired sizes may be delivered in approximately required amounts to a stationary plant for processing. In such a plan, excavating pump dredges might deliver to underwater stock piles and the material be repumped later to the plant, by another pump dredge.

An operating plan of this kind is not necessarily uneconomical. Excess materials may be discarded at the source by selection; rehandling hydraulically is an efficient method of washing out clay impurities; and, in rehandling, the relay pump will transport a much higher percentage of solids than the usual 8 to 12 pct of solids transported by an excavating pump.

Combinations of the various classifications of excavating equipment are often used. Hydraulic methods of excavation similar to practices in the land-pebble phosphate fields of Florida are sometimes employed, whereby high-pressure hydraulic monitors sluice the materials into sumps from which hydraulic pumps deliver to the processing plant.

Certain deposits contain an excess of boulders requiring crushing, notably the alluvial-fan deposits of the West Coast and the river deposits in the Pittsburgh, Pennsylvania, area. These deposits sometimes contain a relatively low percentage of sand. On the West Coast, special markets have been developed for crushed gravel (called crushed rock) and the practice generally is to construct dual plants to produce unwashed, crushed gravel in various sizes along with washed, uncrushed gravel and sand. In certain areas, unsound material prevails in some size ranges only and selective digging is practiced. In a great number of plants, small percentages of boulder sizes, say not more than 5 pct of the total material, are usually rejected at the receiving hopper.

In any plan of development, it is important, in view of current specification trends, that the prospective plant operator know the availability of minus 50-mesh and minus 100-mesh sand particles and their location in the deposit, or their availability from other near-by sources; otherwise he may be soon faced with the difficult problem of preparation of fines by crushing or other methods. The alternative, assuming that these fine particles exist in desired quantity throughout a deposit, may be expensive methods of recovery.

Presence of deleterious materials will influence development methods even to the point of requiring preliminary washing by means of hydraulic excavation, to be followed by dewatering and transportation to the plant by other means. Preliminary desanding and trash-removal tipples are often used to receive the discharge of dredge pumps. These units usually are set up alongside the excavation and throw out sand and trash by the centrifugal, swirling action of the water within an old pump shell, or other device. Being effective in discarding sand excesses, they are a means of eliminating excessive transportation costs in the plant. After removal of excess sand and trash, a relay pump dredge or truck equipment delivers the product to the plant.

Deposits may be thin or they may be very thick. Where beds are relatively thin, the working face is rapidly being extended and great acreage may be depleted in relatively short time. Mobility is then required. Long, sectionalized field conveyors fed from a movable hopper adjacent to the working face are sometimes used under those conditions, and recently semiportable plants of bolted construction, or portable plants, have been adopted where length of haul is excessive. In an extreme case, a rail-mounted plant follows the workings as they progress.

Thick deposits may justify the working of more than one level but that practice is not generally applied. Variations in the grading of material as depth increases often determine the plan of excavation. Not infrequently, a deposit has fine sand near the top and the size increases with depth; then there comes small gravel, which, in turn, progresses uniformly downward to the coarser sizes.

Stripping

Removal of overburden often presents a complicating operating problem but sometimes is insignificant. Underwater deposits have no stripping, although undesirable material may at times be deposited during flood periods over the top of an otherwise excellent deposit, requiring that steps be taken to divert river currents by jetties or other means. Practically all land deposits are covered by overburden, of various thicknesses. Light, sandy overburden, particularly in dredging operations, sometimes is put through the plant together with the sand and gravel and is then washed out during processing, but it is good practice, when overburden is not easily removed by washing, to strip ahead of excavation.

Stripping is done at intervals as required or may proceed concurrently with excavation of sand and gravel. The same equipment may be employed for both stripping and excavation, depending upon the extent of the overburden and the size of the operation. Alternating stripping operations with excavation, using the same equipment, is sometimes practiced. Heavy thicknesses of unsalable overburden must be removed and disposed of economically; otherwise an excellent deposit sometimes has little commercial value.

Large earth-moving, tractor-combination machines of the types employed by contractors are being used for removal of overburden and sometimes for excavation of sand and gravel. Some of these machines, usually caterpillar-mounted and diesel-powered, combine excavation, haulage, and dumping in the disposal of 12 cu yd or more of material per load. It is not uncommon, where overburden is heavy, for stripping to be done on contract by others than the operators of the deposit.

Overburden and the excesses and deposition coming from wash water are waste products of plant operation that present disposal problems. Overburden is generally dumped or cast into worked-out areas while plant wastes are accumulated in settling ponds and excess sizes are stock-piled. Often changing emphasis in markets will at some later time result in sales for so-called "waste" sizes. During the recent war, when new construction was virtually at a standstill, a large eastern operation processed asphalt sand from a 30-yr accumulation of fines that had been allowed to settle out as waste from the plant wash water in a worked-out area. This waste had a high percentage of required fines whereas unexcavated material in the bank had insufficient fine particles to meet specifications. In plants where there is large accumulation of excesses, it is good practice under some circumstances to install dredge-type pumps, fed from sump boxes, for disposal of waste at some distance from the deposit.

Delivery

The quantity of materials to be processed daily will determine to a large extent the development procedure to be followed. Plants vary in size from those producing a few tons per hour of one or two grades to plants of 700 to 1000 tons per hour producing 15 or more grades of material. Large plants require heavy capital investment in power excavating machinery, conveying equipment, washers, screens, crushers and classifiers, while the smallest plants may need only a gravity screen or single washer fed by a scraper or truck.

Method of delivery to the processing plant depends upon surface topography and the type of excavating equipment employed. Utilization of gravity in processing is desirable and necessitates elevation of the materials to the head of the plant, from which the material flows to the successive processing steps one below the other by gravity. Excesses of sand sometimes are disposed of through washing as a preliminary to elevation, in order to conserve power. Pump dredges, under certain conditions, discharge into sumps for disposal of excess fines and water prior to elevation of the material to the plant.

Haulage from dry surface deposits may be by trucks, locomotives and cars, conveyor belts, hydraulic pumps and pipe lines, or, on occasion, by large diesel-powered earth movers. Trucks of large capacity are being used because of their flexibility, wherever conditions are favorable. Cableway excavators deliver directly to the top of the plant, as do dredge pumps operating under normal conditions.

Adequate sources of water are necessary to the continued operation of sand and gravel plants and a supply should be guaranteed. Dredged materials delivered in pipe lines sometimes require the addition of outside wash water, for scrubbing and screening, when dirty water is removed in the early stages of processing. Wash water always is required for materials delivered by any other method. Requirements of water for washing have increased over the years; tighter specifications govern the cleanliness of the product, and water is an aid to the settling and recovery of fine sand particles, which can be best effected if interference to settling from clay particles contained in the voids be first minimized. Common practice of carrying water from the early stages in processing down through successive operations, together with the dirt it carries, should be discontinued in favor of adding clear water at the various processing units. A rough rule used by producers for the minimum water required is one gallon per minute for one ton per 10-hr day of finished product.

Many an operation has been sorely pressed for water during periods of drought and some have been closed down because of the lack of it.

Frequently, wash water is run into settling areas, or even thickeners, to be clarified for re-use.

MINING METHODS

Characteristics of a deposit may restrict the choice of method and equipment for excavation and haulage, but ordinarily most deposits can be excavated by more than one practice, employing various kinds of excavating equipment and haulage units. A deposit covering a lake bed might be an exception and may limit the choice to hydraulic pump excavation and loading into barges. In general, there is no formula to associate a single class of equipment and mining method with a specific type of deposit; several methods may prove successful.

The overburden covering nearly all pit and bank deposits has a bearing on the selection of suitable mining procedure. If the topsoil covering is thin, it may be removed in the process of excavation, and under some conditions may be permitted to pass through the processing plant and be removed by washing. If thick enough to hamper excavation, practice is to remove it separately. The stripping may proceed to parallel the excavating methods, using the same or separate equipment, or may be entirely separated from the excavating procedure.

Bank deposits are excavated dry and haulage from bank deposits is nearly always on the level or downgrade to the plant, thus providing for minimum power consumption in transportation. Ordinarily these deposits are mined by power shovels, making a single cut into the face. Multiple "bench" mining has been recommended for faces higher than 50 ft, because of the danger of caving, but the practice is seldom followed in preference to working single high benches, as the latter permit the use of larger shovel units, which need be moved less frequently and thereby are operated with increased efficiency. Scarifiers of heavy steel rail are successfully operated on the West Coast to cave material from banks as high as 100 ft in advance of a shovel, to bring material down for loading and to protect the shovel from cave-ins. The scarifier, a drag affair much like drags used for preparing the soil in road construction, is hung from a dragline on top of the bank and is manipulated vertically against the face. High banks sometimes are excavated as single benches by power scrapers.

In stripping high bank deposits, overburden generally is removed by power shovel. Hydrauliclicking would be suitable if water under pressure were available. Draglines, power scrapers, or slackline cableways are alternative methods for removal. Usually there are ravines and gulleys associated with bank deposits into which overburden may be dumped. Trucks or cars pulled by locomotives are loaded from shovels and draglines but cableway excavators and scrapers, being delivery units, often can haul to waste in one operation. In truck equipment, the

trend is in the direction of utilizing increasingly large payloads, as much as 15 cu yd or more, hauled in side-dump or end-dump bodies.

Trucks, and sometimes cars pulled by locomotives, are the common haulage units from bank deposits. Field belt conveyors are sometimes used. These conveyors have high first cost but low operating expense.

Very little hydraulicking of bank deposits is now done but the washing advantages inherent to sluicing are being utilized at some bank deposits where clay is a serious contaminant and where power shovels and draglines are the excavating machines. Sluices are the transportation mediums in such plants, where the deposit is higher than the washing plant.

Practice in these operations is to dump excavated material, often containing as much as 20 pct clay, from trucks or cars into a hopper high enough above the washing plant for sufficient gradient (10 to 15 pct) so that clay may be loosened and at least partially emulsified as the material flows through a launder to the plant. Water is introduced into the hopper in great volume; as much as 600 gpm for each ton of sluiced material is required, which is a costly process, particularly when the water must be pumped. In extreme cases of contamination by clay, gravel so transported may in addition be put through revolving scrubbers and yet require the services of men to pick clay at the several conveyor belts comprising the intraplant transportation system.

In excavating bank deposits from above, sometimes called top benching, draglines, slackline cableways, and power scrapers are most commonly used. The same equipment is suitable for stripping overburden—to be cast aside into the excavated area if draglines are used. With draglines so operated, the same types of haulage units are used as in shovel excavation of bank deposits.

Pit excavation is distinguished from bank excavation by the need for elevating material and the possibility of encountering ground water. Such deposits are classified as dry or wet pits according to the absence or presence of subsurface or ground water. Nearly all dry pits are excavated by methods comparable to those practiced in bank excavation. Pit deposits may be excavated by power shovels, draglines from above, dredging, slackline cableways, power scrapers, or hydraulic monitors.

Top benching, as it is sometimes termed, by draglines, is common and economical practice. In sizable operations, draglines with long booms work the deposit according to a parallel cut pattern, casting overburden into worked-out cuts and then excavating gravel without changing position. Slackline-cableway excavators are in common use, both for dry pit and wet pit deposits. The slackline depends upon returning the empty bucket by gravity and the loaded bucket is raised above the surface on the inhaul to dump, usually, into a hopper at the top of the plant.

Caterpillar-mounted tractor combinations are adaptable to stripping under nearly all conditions in dry deposits. Some of them dig, load, and haul to dump while other units of great capacity are principally tractor-pulled haulage units. Diesel-powered, they are economical to operate, and handle tremendous quantities of overburden per day. Often stripping of heavy overburden is done under contract by owners of such equipment, who uncover sufficient deposit for as much as a year's operation of the plant.

An added advantage is that the tractor may be fitted with a bulldozer or angledozer when not stripping and be employed for all kinds of utility work, such as road maintenance and the trimming of stock piles. Sometimes these are used in excavation to carry sand and gravel to flumes for hydraulic sluicing, or to bring down material from high banks to field belt-conveyor hoppers, or in other ways. In a few instances, when a deposit was of relatively loose materials, tractor combinations actually have performed the entire excavation of the sand and gravel and have delivered it to plant field hoppers.

The choice between dragline operation from above a pit deposit, a shovel operating from the pit floor, or other methods is often determined according to the type of haulage that may be selected. Length of haul, grades to be negotiated with full loads, and the possible need for a long roundabout course are factors to be considered in making a decision. Often the relation between depth of pit and area prohibits long, circuitous haulage routes for either trucks or locomotives and, in some operations, the flexibility of trucks is retained by restricting their operations to the pit floor, their loads being usually transferred to inclined belt conveyors. In the crushed-stone industry, there are several comparatively recent installations in which loaded trucks are cable-drawn up grades as steep as 16 pct.

In dry pit deposits, or bank deposits, where transportation by field belt conveyor is the preference and there is a large percentage of boulders, a primary crusher sometimes is operated on the excavation floor near the working face. Usually rail-mounted, the crusher is fed from a pendulum swinging belt conveyor, which is supplied with material from a movable field hopper. The hopper is shifted when needed by the shovel and the main field conveyor is extendable in sections.

Wherever subsurface drainage is insufficient to carry off ground water to a level below the bottom of a gravel deposit, the deposit must be worked as a wet pit. Methods employed for excavation depend upon the height of the water table and also the rate of water flow. Water content in wet pits and the rate of subsurface flow vary according to the imperviousness or porosity of the gravel deposits themselves. Knowledge of these factors is essential before a dredging operation is undertaken, which removes roughly ten parts of water by volume to each unit of

excavated material. This water must be replaced if operations are to continue over any extended period of time.

Wet pits are very often excavated by equipment standing on the ground level above, including draglines and cranes with clamshell or orange-peel buckets. Draglines, power scrapers, slackline cableways and cranes are equally effective for underwater excavation. Overburden from these deposits may be excavated separately or, as often is done, may be caved into the water and washed out. There are a few places where dredge pumps are utilized for stripping cover from old river beds. Where the water level is below the top of the gravel deposit, material often is taken from both above and below the water level. There are places where power shovels excavate the above-water fraction of a stratum and are superseded by dredging to a lower level later. Sometimes, in working deposits below the ground-water level, draglines operate at night to fill hoppers and on the day shift the drained material is conveyed to the plant.

The hydraulic dredge is by far the most commonly used of the dredges, and is used almost to the exclusion of all other methods in some areas of the United States, principally in the south and southeast, where the water table is near the surface. Ladder dredges are the means of excavation in many river operations and in some large-capacity wet pit operations, and clamshell dredges are in limited use.

In many deposits, cutters must be employed to loosen consolidated materials ahead of the pump suction. There are places where draglines work ahead of the dredge; to undercut and cave the bank down into the lake. Hydraulic monitors frequently are mounted on board dredges to play a stream of water against the bank, to cave it ahead of the dredge.

Hydraulic dredges nearly always excavate and deliver material direct to the processing plant, pipe lines usually carrying about 10 pct and sometimes up to 20 pct solids. Diesel engines and electric motors are the principal pump drives. The application of jetting to hydraulic dredge operation is being done successfully in a very few plants to increase enormously the production of standard dredge pumps. In principle, an extension is made to the suction line and an auxiliary pump forces water from below into the annular space between the two pipe cylinders. Passage of this water through a venturi creates a vacuum that literally raises the solids up through the suction line. As much as 60 to 70 pct solids is thus pumped through pipe lines and quantities of material, as much as 800 tons per hour, are excavated and delivered by a 10-in. dredge pump. The 100 pct increase in power consumed thus is sacrificed for a 300 pct increase in production.

Where distance or vertical head necessitates use of booster pumps, a dredge sometimes pumps to a shore location, excess sand is wasted there and the dewatered material is relayed to the plant by trucks, conveyor

belts, or other means. Intermediate reserve storage of unprocessed material is thus provided also. Several dredges may be operated in a single deposit where there are sand pockets, separate gravel-bearing sections, and wide variations in particle sizes, in order to deliver selectively desired proportions of material to the plant. In operations of that nature, the digging pump dredges usually discharge into the "lake" near the plant and there another dredge relays the material from separate underwater stock piles. Material once pumped is loose and the suction line of the relay pump dredge will pick up and then transport probably the total tonnage delivered to it by two similar pumps.

There are other variations in using hydraulic dredges. In deposits containing large percentages of clay, where pumping is difficult, material is sometimes excavated by dragline and sluiced to a dredge pump (see section on Development). In another variation, material is delivered by side-dump cars from a dragline and dumped at the edge of a pond near the plant. Water from a high-pressure standpipe undercuts and washes the material out into the pond, the purpose being to emulsify the clay. A hydraulic dredge then delivers the material, with attendant washing action, to the plant.

Reverse combinations of hydraulic dredges and other excavating equipment sometimes are used. In Minnesota, for example, dredge pumps deliver to sumps at a number of operations and the material is rehandled by slackline cableways, or draglines and trucks deliver to plants.

Towboats and barges are the usual form of delivery from ladder dredges to land plants, where shore equipment transfers either to a land plant for further processing, or to distribution bins if the material is processed on the dredge. Fig 3 shows the plan and elevation of a large-capacity ladder dredge.

In marine deposits, river, lake, and ocean, subaqueous mining is the common method of recovery and dredges are employed as a rule. Such floating equipment must be able to withstand floods or wave action, and in ocean deposits be flexible to compensate for tide variations and be designed to resist the corrosive action of salt water.

River beds and small islands can be excavated by slackline cableways on the river bank or by dredges. In river operations, dredges must often mine beds at widely scattered points, so that there is preference for towboats and barges for transportation. Many river dredges of the ladder type are built to wash and screen material.

River bars are customarily dredged selectively, dredges being alternated between a number of bars according to the type of product required for market. The hydraulic pump dredge is in common use. Ladder dredges are employed frequently where extensive bars are under excavation. Clamshell dredges are limited to use where the water is excessively deep or where boulders and logs are complicating factors.

PREPARATION FOR MARKET

It is in the preparation of sand and gravel for market that the industry has undergone pronounced change since the first edition of INDUSTRIAL MINERAL AND ROCKS was published in 1937. Since that time the industry has become much more scientific in processing than was necessary in earlier years. The majority of plants necessarily have much more equipment and must have great flexibility, often requiring great

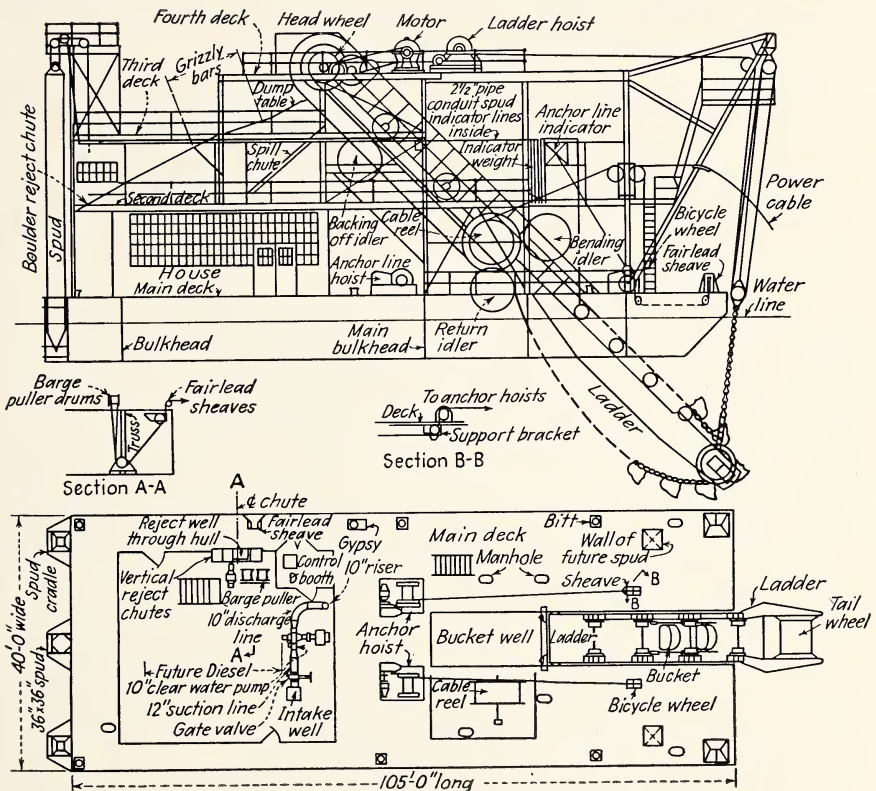


FIG 3—ELEVATION AND PLAN OF CONTINUOUS BUCKET LADDER DREDGE.

ingenuity in order to comply with modern requirements of production.

Methods and equipment for the production of sand and gravel necessarily vary widely according to the method of excavation, nature of the material as it occurs in the deposit, and the demands of the market in which the products are to be sold. Market requirements as determined by specifications and the number and variety of sizes demanded for various applications have had the greatest influence on trends in production. The result has been great increase in the number of equipment units in a plant and new concepts of production, as indicated by the flowsheets of new and modernized plants.

Plant layouts have recognized past inefficiencies in production. The

industry is highly competitive within itself and is meeting competition, through economical operation, from crushed stone, crushed slag, and other construction materials. It can be said that the day when haphazard, uneconomical production was permissible has passed and that the modern plant must be arranged, where its deposits require, to enable substantial improvement of materials at hand as laid down by nature. That the industry has made its plant operations more economical is proved by the almost insignificant price increases for its products during these years of inflated costs, when most commodities for use in construction (1947) have approximately doubled in price.

The industry still has many simple plant layouts, as it did 10 years ago, where production is modest and of one or two grades from deposits that present no particular complications, but the large bulk of the tonnage nationally is not produced in such plants. Our discussion and the selection of flowsheets and plant layouts shown herewith are therefore largely representative of more modern production principles to meet present-day requirements.

The simplest plants are those that produce sand with little or no gravel. A typical flowsheet would consist of a pump dredge, a stationary screen to remove trash and gravel to waste, and a hopper to receive the sand and water passing the screen. The hopper may be of V-section with three or four openings toward the bottom closed by gates that are hand-operated. A flume passing over the hopper has three or four openings in the bottom and occasionally is operated to effect a rough size classification. When gravel is present in sufficient quantity, the oversize from the preliminary screen may be passed over other screens to produce one or more sizes of gravel.

For processing larger tonnages containing a considerable proportion of gravel, more equipment units are required, including a scalping screen, crusher for oversize, more area of screening surface, and sand-settling machinery. With a hydraulic dredge, material would be delivered to the scalping screen, through pipe line by way of a spread table or surge box in "dry" operations, by belt conveyor, bucket elevator, crane, or slackline cableway. Wash water, except possibly where there is dredge-pipe delivery, would be applied over the scalping screen or at the point of discharge over that screen.

For capacities up to several hundred tons per hour, the number of processing units is increased proportionately. Greater screening surface would be essential to handle greater tonnage and more screen units in series, or parallel banks in series, would be needed for making more sizes of gravel. Similarly, there would be several crushers, operated in parallel for reasons of capacity or for progressive stage reduction.

One crusher would receive the largest oversize cobbles while a second would receive the oversize gravel from other screens and be

operated in closed circuit with those screens. There would be a third crushing unit, and so on, depending upon the range of sizes of gravel produced, the percentage of crushed gravel desired, and overall tonnage. Fig 4 is representative of a plant layout for the production of a maximum of crushed products. Sand washers and recovery equipment needed would be in proportion to tonnage handled, and, in the larger plants, there is much dewatering equipment and many crushers for production of gravel in the finer size ranges. Commonly used sand-processing equipment includes rake and screw washers, simple settling tanks, automatic-

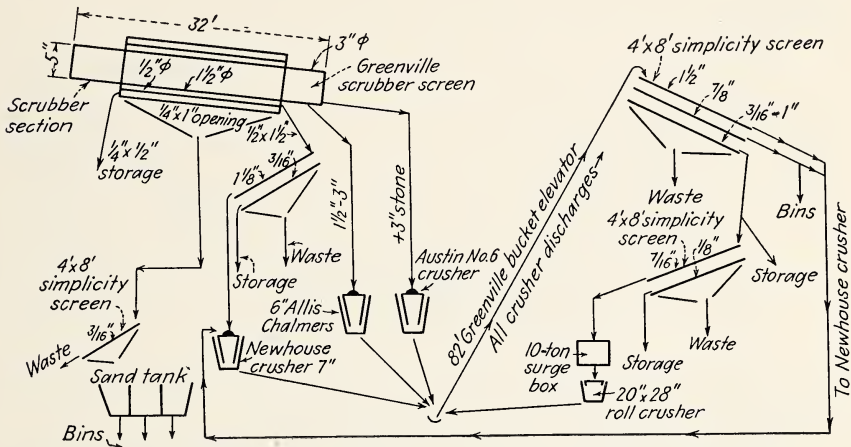


FIG 4—PLANT LAYOUT FOR HIGH-PROPORTION OF CRUSHED GRAVEL SIZES.

discharge sand tanks, rising-water current classifiers, large settling boxes, and bowl classifiers.

The majority of plants have processing equipment superimposed over plant bins for direct loading into trucks or railroad cars, and, as a rule, gravity flow is utilized to the fullest extent throughout in material flow. Crushers may be mounted in the plant structure or on the ground below, and belt conveyors and bucket elevators are commonly used for intraplant transfer. The trend is decidedly in favor of belt conveyors, because of low maintenance, where plant layout and space will permit their installation.

Very large dredges often have the screening and washing plant on the dredge itself; some also have on board crushing plants and complete sand plants, including rake or bowl classifying equipment, so that completely finished products are delivered into separate barges by felt conveyors.

Dry-land plants designed for slackline cableway excavation commonly have a grizzly at the top, over which the bucket discharges. The oversize pieces roll off to a chute delivering to a crusher bin. The

crusher would be in closed circuit with a screen. A typical flowsheet of slackline cableway operation is represented by Fig 5.

Many of the very large plants employ power shovel and dragline excavation, with either truck or locomotive and car delivery to a hopper from which an inclined belt conveyor transports the material to the head of the plant. Where many large boulders or cobble sizes are encountered, accepted practice is to put them through a primary crusher below the hopper. Oversize coming off a grizzly above the hopper would be put through the crusher to join the fraction by-passed on the belt con-

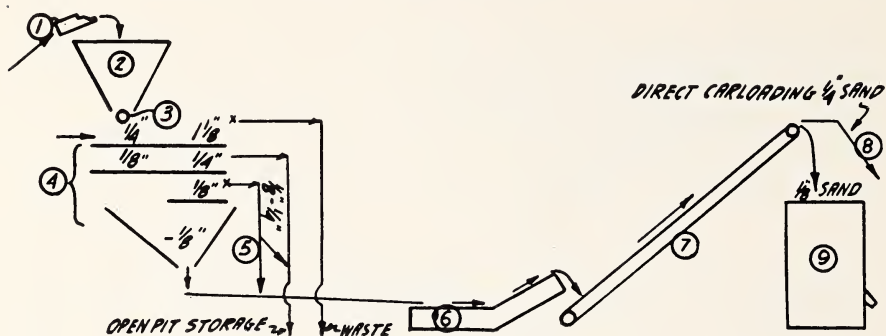


FIG 5—SLACKLINE CABLEWAY LAYOUT.

veyor. If oversize material is little in quantity, it is often delivered to the plant by belt conveyor directly from the shovel.

Certain deposits have so many boulders and cobbles that plant operation is essentially a rock-crushing problem and the actual production of sand and gravel as such may even be incidental. Deposits of that nature are found on the Pacific Coast and in parts of the Midwest. A typical California plant, operating from an alluvial fan deposit, is often a dual operation. Pit-run material is split and the gravel and sand are screened and washed through one plant while, alongside, unwashed crushed-rock sizes are produced.

The foregoing has dealt principally with basic considerations that are still fundamental in the present age of producing many sizes and grades of material. There are many variations in plant design and selection of equipment in the plants of the 1940s to perform the functions discussed. Where contaminated materials are present, log washers, drum-type cylindrical scrubbers, and belt pickers are employed. No attempt is made herein to consider various types of feeders and other auxiliary equipment, which, while not basic production units, nevertheless figure importantly in economical plant operation.

A discussion of this nature would be far from complete without a consideration of factors that have changed the concepts of plant production in recent years and the methods of operation that have had to be perfected as new and more rigid requirements have evolved.

More specifications and tougher requirements for the grading and quality of sand and gravel are the principal factors that have made production more involved, and there are trends toward increasingly rigid requirements yet to be met generally.

A few years back, an average-sized plant was concerned only with producing four or five sizes of gravel and usually a concrete sand and a mason's sand. Today, that plant often is called upon to produce as many as 15 sizes of gravel, owing to differences in grading requirements set by various purchasers and the extension of markets for sand and gravel. Significant progress is being made toward the standardization of aggregate sizes used for similar purposes (see later section on Specifications) but multiple sizes for various uses and users will continue to constitute a production problem.

The problem of producing multiple sizes is complicated further in plants so located that they ship into several states and must satisfy a number of federal, state, county, and city specifications simultaneously.

Not only is there greater demand for more sizes of gravel but many specifications call for a 100 pct crushed product of a given size or for certain percentages of crushed particles within a size classification. There may be just a minimum set—for instance, a 40 pct crushed gravel—or the percentage may be established within maximum and minimum limits.

A typical specification for railroad ballast requires that 100 pct pass a screen with 2-in. square openings, 15 pct be retained on $1\frac{1}{2}$ -in., 20 to 30 pct be plus 1-in. and 15 pct be the permissible maximum fraction passing a No. 4 sieve. The product must be washed and from 41 to 100 pct be crushed. Another railroad specification will require that 80 pct of the product be crushed; another may demand that the specific gravity of the material be at least 2.80; still another will specify that a washed gravel ballast have 15 to 20 pct sand, or that the product be graded through a revolving screen.

Engineers that write specifications must, of course, consider the materials at hand as they are available to plant operators and they sometimes do where deviation from "ideal" specifications, which cannot be met, will yet accomplish desired results. In Mississippi, for example, where there is little large gravel, highway specifications were rewritten several years ago so as not to require that gravel be crushed.

There are other special specifications that are being satisfied. For example, a producer was called upon to deliver a special small size of gravel for use in making a porous concrete for slope revetment work on a federal project. It was specified that no more than 5 pct by weight be retained on $\frac{3}{4}$ -in. square screen openings, that 10 to 60 pct be retained on $\frac{3}{8}$ -in. screen openings, 82 to 90 pct on a No. 4 sieve and not less than 95 pct be retained on a No. 8 screen sieve. No sand was per-

missible, necessitating that a crushed sand size be produced separate from the natural sand flow.

Filter, engine and sandblast sands, produced by a few sand and gravel plants, sometimes must be graded by dry screening. In metropolitan areas, certain classes of users require a dry-processed sand of building grade like New York's Cow Bay sand, which must be produced simultaneously with a wet-washed sand of the same size and many other grades. The foregoing are mentioned to emphasize some of the typical problems confronting producers of sand and gravel.

Typical sizes produced in a recently renovated large eastern plant that operates a bank deposit heavily predominating in sand and small gravel are: $\frac{1}{10}$ to $\frac{3}{16}$ -in., $\frac{3}{16}$ to $\frac{1}{4}$ -in., $\frac{1}{4}$ to $\frac{1}{2}$ -in., $\frac{1}{2}$ to $\frac{3}{4}$ -in., $\frac{3}{4}$ to $1\frac{1}{4}$ -in., $1\frac{1}{4}$ to $1\frac{1}{2}$ -in., $1\frac{1}{4}$ to 2-in., minus $\frac{1}{10}$ -in. dry brick or plaster sand, minus $\frac{1}{10}$ -in. washed sand, asphalt sand (25 pct minus 80-mesh), concrete sand blended from the $\frac{1}{10}$ -in. minus sand and $\frac{1}{10}$ to $\frac{3}{16}$ -in. gravel. This plant also maintains stock piles as reserves against pit breakdowns and utilizes tunnel belt conveyors.

In other plants serving a variety of markets, the range in sizes is just as imposing although usually in larger sizes. To complicate plant operation further, radical changes in markets sometimes occur. When priority was given almost exclusively to home building immediately following World War II, the demand nationally for sand and small sizes of gravel taxed the ability of the industry to produce, where normally those ranges in size were overabundant. The result was an overaccumulation of gravel sizes in stock piles, some of which were re-crushed into finer sizes. Railroads, in their ballast specifications, want smaller top sizes than heretofore in order to obtain more crushed particles. Another reason is that raises on roadbeds are now being made in terms of fractions of inches, which can be attained more easily with smaller ballast sizes.

Tightened control over plant operation is necessary also because very often plants must produce within closer size tolerances than heretofore in order to avoid rejections. Uniformity clauses are written into many specifications, clauses that restrict variations in grading more closely than specifications that stipulate the percentage within two consecutive sieve sizes, even though all the product shipped falls within the upper and lower limits specified for a given fraction. As a rule, the production of two or three sizes of coarse aggregates for construction of large single projects is required and there is a trend toward requirement of three sizes, partly because of a desire on the part of users to minimize segregation.

Developments like the foregoing have had a profound influence on plant design. It has been necessary to rebuild plants to produce increas-

ingly larger proportions of the finer sizes of gravel, requiring more crushing equipment, greater numbers of screens and very flexible arrangements of machinery, chutes, and blending operations.

Quality standards, from the standpoint of soundness and toughness, are increasingly difficult to meet (see Specifications). Some deposits have been rejected entirely because of requirements for greater quality, while at others great investment for equipment and selective excavation have combined to yield an acceptable product.

Some shales, loosely bound sandstones, argillaceous sandstones, and limestones, ochers, and other rocks, are typical of unsound aggregate pieces encountered. For example, in a certain area, soft sandstone occurs principally in the sizes of gravel larger than 5 in. Selective dredging and the use of special equipment to break down and remove unsound particles have been adopted under certain conditions like this with satisfactory results. Some river gravels consisting principally of cherts have been rejected for grade A concrete highway construction because of poor resistance to freezing and thawing. Stock-piling of such aggregates prior to use is believed to very greatly increase the durability of the concrete, since the degree of saturation is important and, when once dried out, the particles do not readily become saturated.

Not only must soundness of sand and gravel be considered, but shapes of particles and mineral composition are properties under critical examination by some specifying bodies. Elongated particles and slivers are presumed to make plastic concrete hard to work, and they are not preferred in bituminous concrete. Surface texture in its relation to adhesion of bitumen is a consideration provided for in some specifications.

Probably the most difficult problem in plant operation faced by engineers and plant operators is that presented in producing concrete sand requiring as much as 10 to 15 pct of minus 50-mesh particles and 2 to 4 pct minus 100-mesh. Until recent years, lower percentages of minus 50-mesh particles were permitted in all specifications and no definite percentage through 100-mesh was specified. A nationwide study of past grading analyses conducted by the National Sand and Gravel Association disclosed that 61 pct of the 214 sources had less than 2 pct of minus 100-mesh material in the product. With specifications calling for over 2 pct becoming routine, it has become necessary for the majority of producers to modify plant practice.

Large volume of water employed for washing material is a complicating factor, since quantities of valuable fines are carried to waste in the process. There also are a great number of operations where fines are unattainable. Practices to meet such specifications and others to meet requirements for separated sand sizes are discussed later.

TRENDS IN PLANT DESIGN

Productive capacity of the sand and gravel industry as a whole has probably increased during the past several years but in many plants there has been a tendency away from volume considerations in favor of plant design to meet rigid specifications at lowered costs.

Problems such as those presented in the foregoing paragraphs have been reflected in plant designs that are establishing new production trends. The modern plant design must consider quality of product as to grading and cleanliness; low operating cost, with particular attention to minimum manual attention, good unit power consumption, and low maintenance costs; flexibility and the ability to produce and stock a wide number of products; ample space and headroom throughout to accommodate chutes and provide for future additions of equipment; all while obtaining an investment per ton of capacity consistent with local conditions.

Newer plants are being built to hold processing operations as near to ground level as practicable and to provide for elevating only the materials requiring further processing. There also is a tendency to stockpile unprocessed materials near the plant, which is a step in the right direction. Finished materials in large stock piles represent considerable capital investment and nearly always a danger exists that certain finished materials might move more slowly than anticipated at the time they were produced—then there would be the added cost of rehandling and reprocessing.

On the other hand, large reserves of unprocessed materials permit flexibility in the grading through the plant. Reserves also serve the useful functions of protection against interruptions to operation caused by breakdowns in pit operations and permit staggering of the excavating and plant operations.

There also is a tendency to increase greatly the storage capacity for finished products. In plants with bins, arrangement of the individual storage units often is in one or more rows, so that the product from any bin may be loaded out over a long, common belt conveyor into railroad cars, into trucks direct or by way of truck-loading bins. More important, different gradings of materials may be blended from the several bins in loading, to meet certain size specifications. That is one successful method to meet specifications requiring specific percentages of crushed particles in a given size. Some plants have bins especially for separated sizes required for particular projects, which are combined on the blending belt. The drawoff bin gates usually are adjustable.

Many new, large plants provide for tremendous ground storage capacity instead of bins, utilizing tunnel belt conveyors for reclamation and blending. Ten or more grades of material are being stock-piled in

a row over a single tunnel belt conveyor in some plants. In addition, a large tonnage of pit-run materials may be provided near the same plant. Fig 6 shows a modern plant designed for tunnel belt loading out from ground-surface stock piles.

Radial storage systems in which the screening and washing plant are superimposed over a central tower from which radiating bulkheads provide ground storage for a half dozen grades of finished materials have come into wide use. The crushing usually is done on ground level and materials to be washed and screened are delivered to the head of the plant by inclined belt conveyor.

Plants with large ground storage facilities, of which this type of plant is one, have many advantages. Adjustable gates inside the cylindrical tower, in this particular adaptation, are manipulated from above by the plant operator to permit drawoff of free-flowing stocked materials from any compartment onto an inclined loading-out belt conveyor, or the blending of two or more grades in any proportion on the belt. Power-operated scrapers or bulldozers are commonly used to extend the stock piles to any limit out from the center of the plant and it is not uncommon to have several hundred thousand tons in dead storage. The same auxiliary equipment returns the material to live storage as needed. A radial storage system in a plant operating a deposit extremely high in sand is shown diagrammatically in Fig 7. The loading-out belt conveyor usually has capacity in excess of production capacity.

Materials stored in open stock piles for any length of time generally are passed over a rinsing screen as they are loaded for shipment. In western plants, where crushed gravel is produced separately from uncrushed gravel, it is not uncommon to have reserve surge stock piles of unprocessed gravel for each production unit. Use of intermediate storage systems from hydraulic excavations has been touched upon under the headings of Development and Mining.

An eastern plant designed and built by recognized technical experts in the sand and gravel industry is an excellent example of the flexibility that may be attained through provision for large storage piles. With a productive capacity in the 500 tons per hour range, storage for 12,000 tons of pit-run material was provided over a tunnel belt conveyor for delivery to the plant, as a precaution against breakdown in the pit and also to balance pit production with plant requirements. In addition, storage for 100,000 tons of reclaimable finished products was provided in large bins and stock piles alongside, here again served by loading-out tunnel belt conveyors, but for direct loading of ocean-going barges. Either the pit, the plant, or the loading operations can be operated separately or in any combination. During World War II, with its manpower shortages, the same work crew performed all three functions, but not simultaneously.

It has become recognized that greatest efficiency in plant operation is attainable if the plant is kept loaded at a uniform high rate of production throughout. To accomplish that end, surge piles of various capacities are often provided for feed to the primary plant belt conveyor in order to minimize fluctuations due to spasmodic delivery from the excavation. Electrically interlocked belt conveyors and elevators

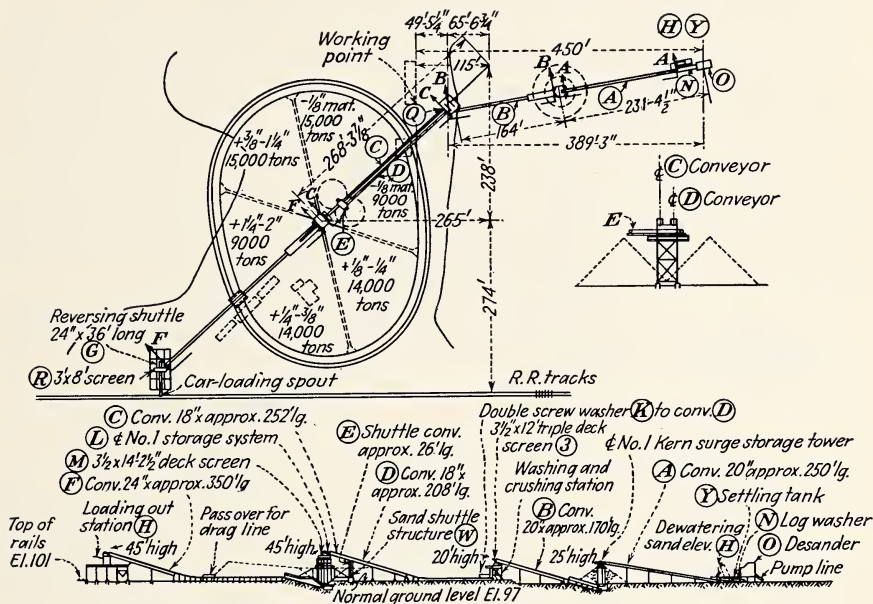


FIG 7—DREDGING PLANT WITH RADIAL GROUND STORAGE SYSTEM.

often are installed, whereby if a production unit stops, all other equipment preceding will stop automatically and in reverse sequence. Increasingly wider use of feeders is being adopted as an aid to control of material flow.

PRODUCING FINE SAND

Trends to requiring higher percentages of minus 50-mesh fines and from 2 to 4 pct minus 100-mesh in concrete sand are fast being entrenched, and many producers have never had anything like such amounts of fines in their commercial products. In many operations, it is simple to recover minus 50-mesh and minus 100-mesh particles in required amounts because they are plentiful in the deposits under work, but in others, particularly in river deposits, they are scarce and sometimes almost totally lacking.

Recommendations of the American Society for Testing Materials

(designation C33-46) for grading of fine concrete aggregate are typical, and are:

Sieve	Percentage Passing, by Weight
$\frac{3}{8}$ -in.	100
No. 4	95-100
No. 16	45-80
No. 50	10-30
No. 100	2-10

In applying this specification, the limitations on the material passing the No. 50 and No. 100 sieves may be 5 to 30 and 0 to 10 pct, respectively, at the approval of the engineer, when the fine aggregate is to be used in concrete mixtures containing five or more sacks of cement per cubic yard. Otherwise, where there is failure to pass minimum requirements for particles passing the No. 50 or No. 100 sieve, or both, the fine aggregate may be used, provided a satisfactory inorganic fine material is added to correct for the difference in grading.

The specification for grading fine aggregates applied by the Corps of Engineers, U. S. Army, is as follows:

Sieve	Percentage Passing, by Weight
No. 4	95-100
No. 8	80-90
No. 16	60-80
No. 30	30-60
No. 50	12-30
No. 100	3.5-10

This particular specification requires that the fineness modulus be between 2.40 and 2.90 and establishes a uniformity allowance of ± 0.10 from an average figure for test samples previously tested. The fineness modulus is calculated by adding the cumulative percentages of sizes retained on the several sieves and dividing by 100.

Such requirements generally necessitate plant modification for greater recovery of the finest particles, while fulfilling the tolerances allowable between intermediate sieves, and very often involve simultaneously reducing the percentage of particles between 16 and 50-mesh. Many sands bulk in that range of sizes.

In any plant, analysis of the material carried away by the wasted wash water will be helpful in determining whether or not the desired extreme fines are present and, if so, whether in sufficient quantity to be recoverable. Oftentimes simple adjustments to sand-settling tanks, or the extension and increase in depth and width of launders so that finer particles will have opportunity to settle in pockets or hoppers, are all that is required. Use of screen wire with different sizes of mesh over

the hoppers is a means of regulating top sizes of sand in simple arrangements such as this. A comparatively simple arrangement for sand recovery is seen in Fig 8. Sand-recovery equipment commonly in use includes simple launder hoppers, tilting boxes or cones, and inverted pyramids. Sand drags, rakes, and screw washers, while often mainly employed as dewaterers, have a part in classification.

In simple arrangements seen by the writer, ordinary launders in combination with sand-collecting hoppers may be used effectively in classification and the retention of fines.

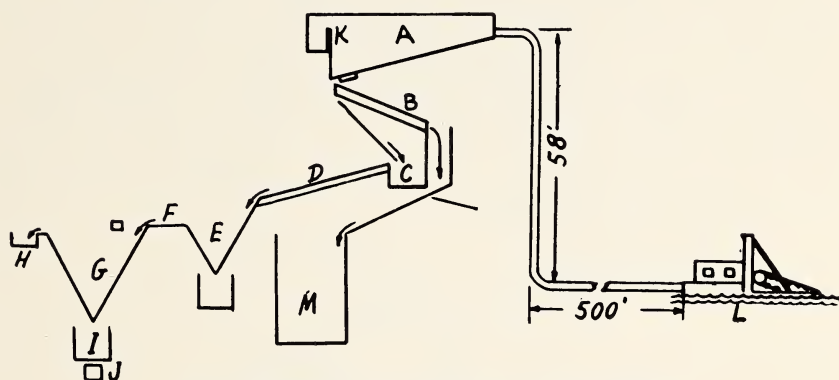


FIG 8—SIMPLE ARRANGEMENT FOR SAND RECOVERY.

- | | | |
|--------------------------|----------------------|--------------------|
| A. Primary settling box. | F. Flume to cones G. | K. Adjustable dam. |
| B. Screen. | H. Waste flume. | L. Dredge. |
| C. Settling box. | I. Tank. | M. Gravel bin. |
| D. Flume to tank E. | J. Sand pump. | |

As a typical example, where minus $\frac{1}{4}$ -in. material is to be processed into concrete sand and mortar sand, all this material and the water are allowed to fall into a sand box of some 60 tons capacity. One long side of this box of rectangular section would be lower than the opposite side, so that excess water and silt may overflow the lip into a launder to waste.

On the opposite side near the bottom, four or five pipe openings of, say 3-in. diameter, may be opened to permit drawing off sand into a launder probably 2 ft wide and 18 in. deep and sloped 3 or 4 pct. Fresh water would be introduced at the high end to wash the material down the launder. A 3 or 4-cu yd concrete sand hopper without screen above and, farther on, a second hopper with fine wire on top, say 0.093-in. square openings, would catch mortar sand. Varying the quantity of water introduced at the head of the flume would control the velocity of flow and therefore regulate the sand recovery. Several sharp bends in the flume in opposite directions would aid in keeping the material in suspension. The valves on the pipe openings could be manipulated ac-

cording to the coarseness of sand particles, and widening the flume out over the mortar sand hopper helps to slow the flow and settle more of the particles.

Where clay is prevalent, large quantities of water are required for washing and dilution, so that the clay does not remain in the voids to interfere with normal settling of sand grains, but, on the other hand, the larger the volume of water used, the more likelihood there is that the highly valued fines will be flushed to waste. Such a condition sometimes requires the use of large settling areas with adjustable baffles to still the water currents and slow the velocity sufficiently so that the fines will be trapped. Bowl-type classifiers are recommended sometimes because they are equipped with agitators to prevent the settling of mud, and recently there has been installation of large-diameter hydroseparators for recovery of fine sand. In a particular hydroseparator, a 50-ft-diameter machine, the settling area was calculated to settle at No. 160 mesh. The formula used to compute the area required was, for every 100 gpm of water handled:

$$A = \frac{M^2}{1400}$$

where A = the area in square feet,

and M = the mesh of the finest material to be retained.

Feed in this installation is the overflow from a three-compartment concrete sand-settling pit. Recovery of minus 100-mesh particles was increased by 2.5 pct, or 10 tons per hour, on the basis of 400 tons of sand per hour, over that recovered in an already efficient settling pit. With this equipment, most of the 200-mesh particles and a great deal of the 325-mesh particles were recoverable because of the quiet and uniform flow of water over the long circumferential weir. Fines recovered are pumped back into the central compartment of the settling pit for interblending as the sand is reclaimed by an elevator. In producing plastering sand, these extra fines are added into the plant-run product near the point of emergence of the sand drags from the water. The installation has enabled the plant to meet specifications requiring that 2 pct of concrete sand pass 100-mesh, with regularity and uniformity (see Fig 9).

Hindered-current classifiers are frequently used in the classification of sand, hydraulic water introduced from below into these cylindrical machines being the means of separation. These units are automatic-discharge type, a plunger being actuated by a float as the settled material builds up to a certain level. In some plants, as many as seven such units in series are operated, the overflow from each becoming the feed for the second, and so on. In that way, a number of sand fractions are

produced, which can be recombined in any proportions, or excesses in certain size fractions may be easily discarded. Some kind of dewatering device, either rake or screw, is operated in conjunction with such classifiers.

Methods of increasing and adjusting weir lengths are being devised by manufacturers of equipment for application to sand drags,

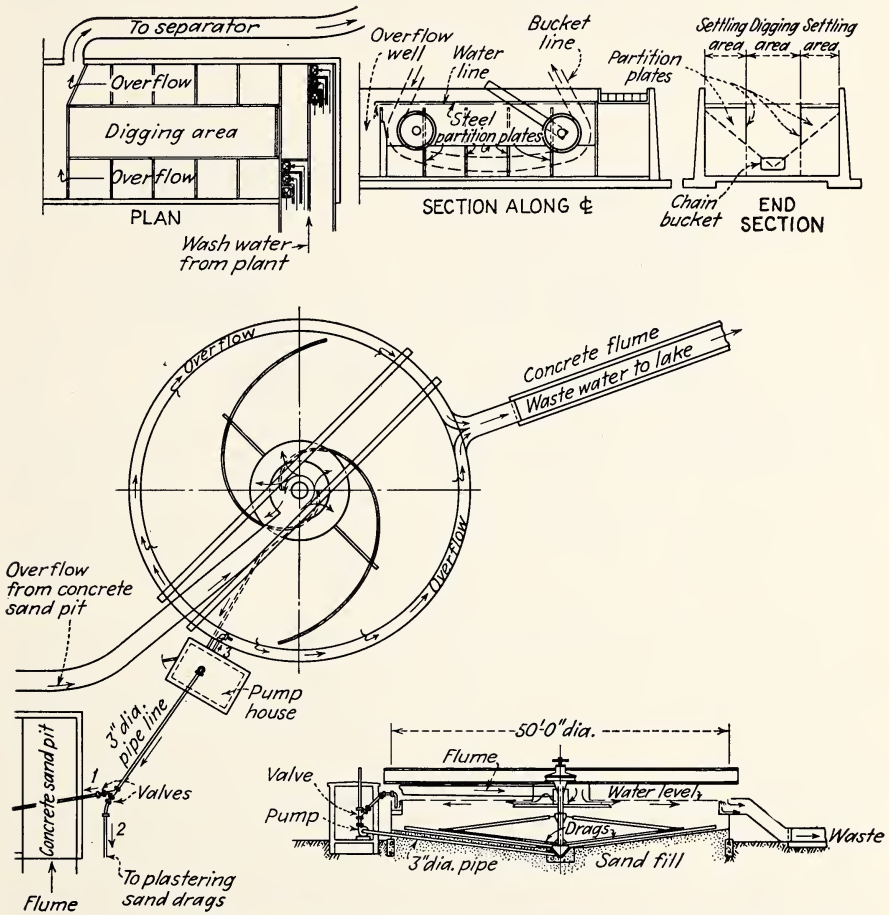


FIG 9—USE OF HYDROSEPARATOR TO SETTLE EXTREME FINES FOR CONCRETE SAND.

screws, or any ordinary settling tanks to increase their effectiveness in fine-sand recovery and to enable them to be operated as classifiers.

If a deposit does not contain necessary fines, as often is true, the only recourse has been to crush or pulverize pea gravel or sand into fines for interblending with the plant-run product, or to interblend a fine sand brought in from an outside source. As an example of the latter practice, the operator of a plant could recover only 7 pct minus

50-mesh particles in concrete sand. The specification required from 8 to 30 pct. Sand from a deposit several miles distant, containing 50 pct minus 50-mesh particles, was interblended on a belt conveyor, 20 pct by weight, to yield a product with 10 to 12 pct fines minus 50-mesh.

The fine-sand problem is so great that it has been suggested that these needed fines be considered as admixtures for concrete to be delivered to the jobsite and proportioned into the mix with a normal concrete sand in desired amounts.

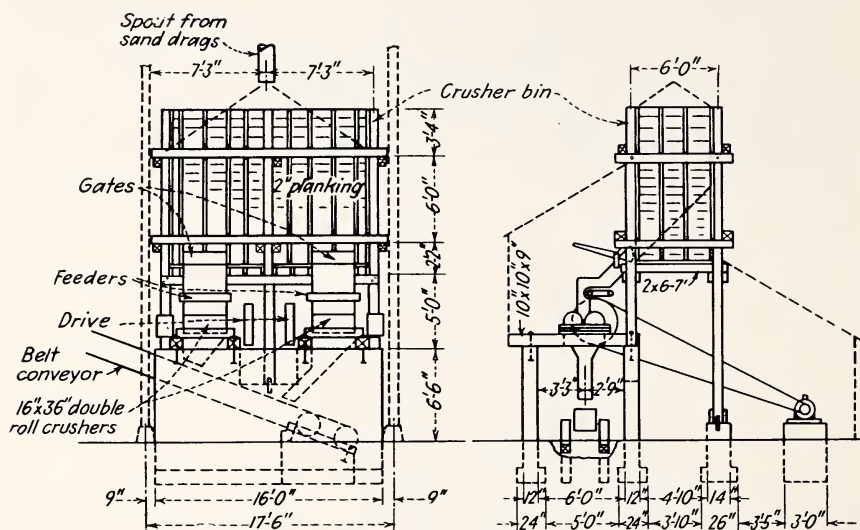


FIG 10—LAYOUT OF PLANT TO CRUSH PEA GRAVEL INTO SAND.

Various methods of producing fines artificially have been incorporated into plants with success. In some operations, pea gravel is reduced to fine-sand sizes by smooth-faced crushing rolls (see Fig 10). Rod mills are also employed, usually in large-capacity operations, and also ball mills, sometimes to reduce a fraction of plant-run sand into fines for recombination with the main bulk. Impact crushers apparently are most widely used for the purpose. These machines may be operated wet or dry and the degree of reduction is largely proportional to the speed of operation. Products of these various auxiliary machines must be classified and dewatered, and usually are intermixed with the natural sand. Maintenance is a factor in these operations and the added cost may be several cents per ton of finished product.

One of the most interesting developments in sand production during the past several years, for a small capacity, has been the adoption of fractionating practices to meet highly rigid specifications. In meeting asphalt-sand requirements for 32 pct by weight to fall within 8 to 40-mesh, 42 pct between 40 and 80-mesh, and 26 pct within 80 to 200-mesh, a plant was designed (Fig 11) to split the sand at 8, 20, 40 and 80-mesh.

Minus 8-mesh feed material was first thickened in dewatering cones and then fed into an eight-compartment sizer, which is in principle a multiple-unit hindered-settling classifier. Rake classifiers served to de-water the selected fractions of sand, graded from coarse to fine in the respective compartments in series. The overflow from the last compartment was recovered in a bowl classifier and the various fractions were interblended in correct proportions. Stock-piled on the ground, a grab bucket placed the several fractions into blending bins. This proc-

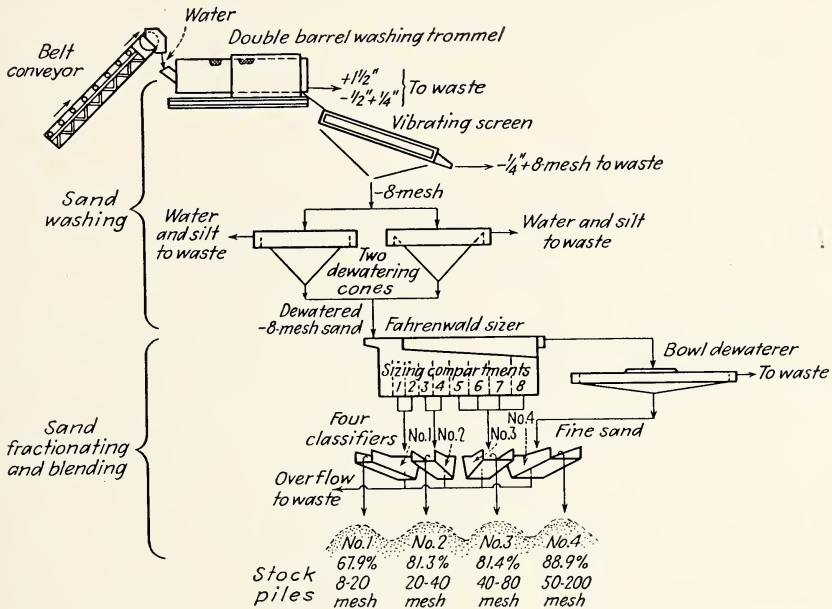


FIG 11—DESIGN OF SMALL PLANT FRACTIONATING FOUR SIZES OF SAND FOR LATER RECOMBINATION INTO COMMERCIAL GRADES.

ess was perfected earlier in producing sand for construction of the Grand Coulee dam and represents the application of metallurgical ore-dressing equipment to the sand and gravel industry.

Some very ingenious and often complex sand-classification plants have been developed, which cannot be described in our allotted space. A flowsheet of an interesting layout is reproduced as an alternative (Fig 12).

Improvement of Quality

In meeting quality standards, the principal operating difficulties are concerned with removal of clay and the so-called unsound and deleterious materials.

Where clay is a serious contaminant, greater than ordinary quantities of wash water are employed and frequently special equipment such

Among the common deleterious materials encountered are carboniferous lignites, disintegrated granite, coal, shale, ocher, soft sandstone and limonite. One or more of these materials may prevail in a given locality and in proportions to threaten the acceptability of a commercial product. Impact-crushing devices are being used with success for breaking down unsound particles in gravel and, to a limited degree, for fine aggregates (sand). Maintenance as a rule is heavy in processing highly siliceous materials. Often a high percentage of passable material is broken down and wasted, but these machines are the most effective corrective device yet developed when operated intelligently. Not only may they process otherwise unacceptable gravel into a passable product but impact crushers have the faculty of "cubing" particles and, in the process of crushing, produce relatively few elongated and slivery particles.

Use of impact crushers has become standard practice in an eastern area where soft sandstone is encountered in river deposits. The majority of unsound particles occur in the larger sizes and river dredges selectively dig materials below 5-in. size insofar as it is practicable to do so. Generally, it is only necessary to put a fraction of the gravel through these machines and that fraction is in the range of sizes subject to rigid abrasion tests before acceptance. The crushers are run at slow or medium speeds, to hold down the production of fines and breakage of sound material. An important reason why some operators bypass as much of the gravel as possible is to prevent formation of too many edges, which would have the reverse effect on the abrasion acceptance test. Abrasion losses (see section on Specifications) have been reduced 25 or 30 pct in the Pittsburgh area and specifications for 100 pct crushed gravel, formerly impossible of attainment, are being met satisfactorily.

In New York state a few years ago, concrete sand was rejected on the basis of unsound particles, so various kinds of eliminators were tried. The result was that so much good material was sacrificed in the process that the deposits in question were abandoned.

In California, a large operation was shut down because of the presence of quantities of disintegrated granite, which made it impossible to meet the abrasion-loss test. To further complicate the problem, not more than 15 pct of the particles were permitted to show evidence of crushing, which meant that the rounded gravel shape of individual particles had to be retained in the product.

A satisfactory product was made by passing the $\frac{5}{8}$ -in. to $3\frac{1}{2}$ -in. size range through a revolving impact drum and screening out to waste the fines through a screen with $\frac{3}{8}$ -in. square screen openings. The eliminator was a 6 by 20-ft drum of $\frac{3}{8}$ -in. steel plate lined with manganese plates. Five 6-in. angle irons the entire length of the drum lifted the

materials as they passed through and dropped them so that impact of particles upon others would break down the soft materials. It was necessary to pass 35 pct of the total tonnage through the eliminator.

An alternative to the use of impact crushers as such for production of particles having desired shape is to use high-speed gyratory crushers and more stages of reduction. Some of the newer designs of plants, where decomposed granites and other objectionable materials prevail, provide for screening out the fines resulting from crushing to waste and thus the soft materials are not permitted to enter the sand stream.

Plant Equipment

Plant processing equipment consists of crushers, screens, scrubbers, sand washers, settling tanks, classifiers of various kinds, and required conveying and elevating machinery. Jaw crushers and gyratory crushers are in commonest use for reduction of large gravel. Jaw crushers generally are preferred in the smaller plants where there are large quantities of boulders, because of low comparative first cost and the large feed opening attainable with modest crusher capacity.

In the large-capacity plants, gyratory crushers are commonly employed for primary reduction. Standard gyratories and cone crushers are widely used in the bigger plants for reduction units. Relatively new designs of the latter, designated "fine bowl" cone crushers, are being used frequently for the production of chips and other small sizes of gravel. Double unit crushers, in which two crushers are in effect incorporated into one machine of the jaw and hammermill types, have recently been put on the market. Rolls are used relatively little as reduction crushers but sometimes are used for purposes like making pea gravel into sand sizes. Impact crushers, incorporated into many plants recently, serve several useful purposes. They may be operated for the elimination of soft particles, for the production of sand from gravel sizes, to improve particle shape, and for general reduction. Two or more of these functions are served in any single installation.

The impact crusher is a variation of a hammermill. Internal rotating cages, or rotors, throw the particles at high speed against breaker plates inside the housing. Fracture occurs upon impact of gravel on the throwing mechanism, on the breaker plates and the impinging of particles on each other. The breaker plates generally are of manganese steel. Speed of rotation determines the rate of reduction and variable-speed means of drive are generally employed. Maintenance is a significant item of cost. Breaker plates are replaceable and it is common plant practice to build them up by welding. High-speed gyratories of newer designs also have the ability to produce particles relatively free from elongations and slivers.

Inclined vibrating screens for sizing materials have largely dis-

placed the use of revolving screens in most plants, although the revolving type is still used extensively for scalping purposes. They do have the favorable property of serving as scrubbers, either as a straight screen or with a blanked-off scrubber section, which is the reason they are preferred for scalping by a number of producers.

Vibrating screens are preferred in nearly all cases, however, because of their high screening efficiency per square foot of surface, the ease in changing screen decks, low headroom required, and low power consumption. There are a great number of vibrating-screen manufacturers and a great variety of designs to impart vibration. There are electromagnetic vibrating screens but nearly all the vibrating screens used in the sand and gravel industry have mechanical vibration and may have one, two, three, or four decks effective for screening a combination of gravel sizes. The majority are inclined screens but a considerable number are horizontal. One of the greatest faults observed in the operation of vibrating screens is the tendency to overload them. Rather than install sufficient capacity in screen surface area, so much volume is often put over a screen that the top layer of the bed of material fed onto a screen has no opportunity to reach the screen cloth and passes on with the oversize.

Usual practice is to take out oversize with the first screen and divert it to crushers while simultaneously removing the sand sizes, with accompanying clay and water, for diversion to the sand-preparation equipment. Gravel sizes are then screened in successive stages, with or without the need for additional crushing, and the only water used is that applied by the sprays over the screens.

Screening surfaces are of woven steel wire or punched plate, the latter being used most frequently where very large sizes of gravel are to be screened. Perforated plate holes may be circular, square, or hexagonal, and there are other shapes available. Stainless-steel wire-mesh cloth is effective for fine sizing. Much study is being given to screen vibration, shape of screen holes and, for wire mesh, to methods of crimping the wire in their effects on the blinding of screens. There is a tendency to use elongated wire mesh for screening critical fine sizes of material, which have an unusual tendency to blind.

Stationary steeply inclined gravity screens are still in service in many hydraulic dredge plants, particularly in the South, and usually where sand is in the majority. Sometimes they are operated with two or three decks.

Grizzlies serve to eliminate excessively large boulders. Stationary types usually are of railroad rails and set on an incline. Other kinds are revolving bar screens or disk grizzlies.

Scrubbers have as their function the loosening of clay from the particles of gravel, so that the clay may later be carried away by a

current of water. The cylinder designs with internal lifters of angle iron, set on an incline, are in common use. There are horizontal types wherein internal spiral blades work the material through. Usually a current of clean water is introduced counterflow to the material. Log washers also are successfully used for clay removal.

A great variety of equipment is in service to recover and classify sand. Ordinary sand boxes or hoppers are frequently employed, as are sand cones, with the discharge from apex gates controlled by the weight or height of the sand settled in the cone. There are the hindered-settling tanks, with rising sorting columns of water, which function as classifiers. Any number of combinations of these common types of equipment are in service to suit the special conditions in a given plant.

Other types of sand-preparation equipment, however, are coming into more favor. In one, the current flows through a long box where the sand is settled and the water and clay flow out over the far end. Settled sand is drawn out by a belt or chain with drags or by reciprocating rakes. Then there are the bowl classifiers, which present a long length of weir to minimize washover of fines, and which have an internal mechanism to gather the settled material to a central drawoff point. In still another type, sand is settled in a circular tank and the excavating is done by an inclined wheel with scoops. The wheel is inclined so that the scoops come up out of the water at one point of their travel and a plow skims off the sand. These several types of machines are sand-recovery units and serve a dewatering function as well, but also are provided with adjustments to control the fineness of the product. Some very elaborate arrangements have been made of equipment in very large plants to produce classified sands to meet rigid specifications.

In less pretentious operations, single sand-recovery units are being made to function as classifiers. Adjustable tailboards on screw and rake washers and the use of rising currents in such equipment are frequently employed, and machinery manufacturers are providing weir designs for such equipment that permit the retention of more fines and, in some cases, a classification.

It is of interest that sand-dewatering wheels are coming back into use with some new adjustments. A wheel turns on a horizontal shaft and buckets dip into a sand-collecting tank to excavate continuously the material that has settled. Adjustments to regulate the gradation of sand are the pitch of the buckets, which is varied to change the digging depth, and the height of the overflow weir. Buckets are perforated to drain off water.

With more complex hydraulic sand-processing arrangements employing large volumes of water, dewatering of the sand for handling by belt conveyor or other means has presented problems. A dewatering belt

conveyor developed in recent years has been applied apparently with success in several plants to transport sand directly from the drainboards of rake classifiers and other equipment to stock piles, or for transfer to conveyors for filling bins or loading. This equipment consists of a short, inclined belt conveyor with skirtboards to confine the sand to a width narrower than the belt, thus building up a loose, filtering bed of sand as it is transported. Water filters out to the sides from under the skirtboards and flows into a gutter.

As was mentioned earlier in this chapter, tractor equipment has come into wide use in the sand and gravel industry. Bulldozers and angledozers have many uses. They transport overburden or gravel in deposits and they are utilized for road maintenance, trimming of stock piles, and in connection with tunnel reclaiming stock-pile systems.

Portable sand and gravel plants have been perfected so that now they can perform many of the functions of the stationary plants economically and it is not uncommon for operators of stationary plants to employ several portable plants to serve large, outlying construction projects.

SPECIFICATIONS

Rigidity of the prevailing specifications and the comparatively great number now effective are the outgrowth of scientific study by users of sand and gravel for concrete highways, buildings, and other structures. They are based largely upon the personal experiences of designing engineers, and the very differences in physical characteristics of materials from different deposits over the country have led to great numbers of varied specifications.

For the purpose of standardizing sizes, to benefit producers and users, the National Sand and Gravel Association, National Crushed Stone Association, and the National Slag Association formed a Joint Technical Committee a number of years ago. This committee, in cooperation with the Division of Simplified Practice of the National Bureau of Standards, drew up recommended standard sizes of aggregates for the specific uses based on sieves with square openings. As approved in June 1936, alternate size groupings designated as A and B were proposed. In the interests of further simplification, Simplified Practice Recommendation R163-39 was released May 25, 1939, providing for a single grouping of standard sizes.

These specifications for specific uses (see Tables 1 and 2) are finding acceptance and form the basis for specifications of such organizations as the American Society for Testing Materials, the American Concrete Institute, the Federal Specifications Board, the American Association of State Highway Officials, certain state highway departments and many other specifying organizations. Their adoption by organizations such as these has been of great benefit to the industry and further

TABLE 1—*Sizes of Coarse Aggregates*
CRUSHED STONE, GRAVEL, AND SLAG

Nominal Size Square Openings ^a		Amounts Finer than Each Laboratory Sieve (Square Openings), Percentage by Weight													
Size No.		3½ in.	3 in.	2½ in.	2 in.	1½ in.	1 in.	¾ in.	½ in.	⅜ in.	No. 4	No. 8	No. 16	No. 50	No. 100
1	3½-1½	90-100 ^b		25-60		0-15		0-5							
2	2½-1½		100	90-100	35-70	0-15		0-5							
24	2½-¾		100	90-100		25-60		0-10	0-5						
3	2-1			100	90-100	35-70	0-15		0-5						
357	2-No. 4			100	95-100		35-70		10-30		0-5				
4	1½-¾				100	90-100	20-55	0-15		0-5					
467	1½-No. 4				100	95-100		35-70		10-30	0-5				
5	1-¾					100	90-100	40-75	15-35	0-15	0-5				
57	1-No. 4					100	90-100		25-60		0-10	0-5			
6	¾-¾						100	90-100	20-55	0-15	0-5				
67	¾-No. 4						100	90-100		20-55	0-10	0-5			
68	¾-No. 8						100	90-100		30-65	5-25	0-5			
7	½-No. 4						100		90-100	40-70	0-15	0-5			
79	½-No. 8						100		90-100	40-75	5-25	0-5			
8	¾-No. 8								100	85-100	10-30	0-10			
9	No. 4-No. 16									100	85-100	10-40	0-10		10-30
10	No. 4-0 ^c									100	85-100			0-10	0-2
G1 ^d	1½-No. 50					100	80-100		50-85		20-40	15-35	5-25		
G2 ^d	1½-No. 8					100	65-100		35-75		10-35	0-10	0-5		
G3 ^d	1½-No. 4					100	60-95		25-50		0-15	0-5			

^a In inches, except where otherwise indicated; numbered sieves are those of the United States Standard Sieve Series.

^b 100 pct finer than 4 inches.

^c Screenings.

^d The requirements for grading depend upon percentage of crushed particles in gravel. Size G1 is for gravel containing 20 pct or less of crushed particles; G2 is for gravel containing more than 20 pct and not more than 40 pct of crushed particles; G3 is for gravel containing crushed particles in excess of 40 pct.

TABLE 2—Typical Uses for Sizes Given in Table 1

[illegible]

² In inches, except where otherwise indicated; numbered sieves are those of the United States Standard Sieve Series.

For plant mixes, the aggregate should consist of appropriate sizes selected from Table 1 combined with suitably graded fine aggregate.

acceptance will simplify production in proportion to their application. Many other size specifications are yet in effect.

Demands for higher percentages of the fine fractions in concrete sand and more uniform grading have resulted largely from experiences of the federal government in building concrete dams and other large structures. On such projects, it was found that use of such concrete sand was instrumental to a better cement factor, greater durability, lower water-cement ratio, lower volume change and reduction in the heat of hydration. Mixes with as low as three sacks of cement per cubic yard of concrete were found satisfactory.

As a result of this experience, many specifying bodies are requiring higher percentages of particles finer than the No. 50 and No. 100-mesh sieves. Relatively high proportions of fines are desirable without question in lean concrete mixes but there is argument as to their necessity in the richer mixes. According to a summary of concrete-road specifications used by state highway departments as of 1941, nine states were requiring a minimum percentage of minus 100-mesh particles, and the range was from 2 to 6 or 2 to 8 pct. As specifications are rewritten, it may be anticipated that more states will require these fines. There is a possibility that the use of modern air-entraining cements may slacken the demand for extreme fines in concrete sand because the small air bubbles entrained in such concrete serve to give plasticity.

Characteristics covered in specifications, other than size and grading, are principally soundness and durability, deleterious particles, and hardness and strength of aggregates. Other characteristics occasionally are covered in some specifications or, if not, are given consideration. Among them may be shape of particle, surface texture, mineral composition, absorption, specific gravity, weight, voids, volume-change characteristics, and possible reactivity with portland cement.

Unsatisfactory service records of concrete structures and attempts to ascertain the causes for premature failure have focused increasing attention on the quality of aggregates and the effects of soft and unsound particles on service behavior. Disintegration of weak, friable aggregate, wide volume changes in coarse aggregates, and chemical reactions between certain aggregates (amorphous or microcrystalline silica) and cements are factors considered responsible for early disintegration of concrete. Principal tests for quality of aggregates are those relating to soundness and hardness or percentage of wear when tested to prescribed standards.

In most principal specifications, both fine and coarse aggregates must pass a sodium sulphate or magnesium sulphate accelerated soundness test (see ASTM Standard Specifications for Concrete Aggregates, C33-44) except that aggregates failing in the accelerated soundness tests may be used if they pass a satisfactory freezing and thawing test.

Permissible losses in the sodium sulphate test are generally 10 pct by weight for sand and 15 pct for gravel in five cycles.

The Los Angeles rattler test for abrasion (a measure of hardness and strength) has almost generally superseded the Deval abrasion test. The Los Angeles test consists of determining the percentage loss, through breakdown, after subjection of coarse aggregate to 500 revolutions in a standard cylindrical drum charged with shot. Average permissible loss for the various state highway departments is 45 pct for concrete aggregates and 40 pct for aggregates used in bituminous work.

Requirements of the state highway departments in compliance with the Los Angeles abrasion test are summarized according to frequency distribution in Table 3.

TABLE 3—*Compliance of State Highway Departments with Los Angeles Abrasion Test*

Percentage of States	Maximum Loss, Concrete Paving, Pct	Other Classes of Pavement or Bases, Pct	
		Highest Limit	Lowest Limit
100	65	75	50
90	50	65	40
80	48	55	40
70	45	50	40
60	40	50	40
50	40	45	37
40	40	45	35
30	35	45	32
20	35	40	25
10	30	40	25
0	28	30	20

A recent summary of Los Angeles rattler-test results compiled by the National Sand and Gravel Association on coarse aggregates from 103 sources was as follows:

Percentage of Sources	Percentage of Wear	Percentage of Sources	Percentage of Wear
100	59.2 ^a	50	31.1 ^a
90	41.2 ^a	40	29.4 ^a
80	37.2 ^a	30	25.6 ^a
70	34.0 ^a	20	23.0 ^a
60	32.9 ^a	10	20.4 ^a

The lowest value was 14.8 pct.

^aOr less.

In general, specification requirements as to permissible percentages of organic impurities, clay or silt, soft friable or otherwise unsound particles, are not nationally standardized. ASTM Standards for all uses of aggregates, however, have a broad influence on specifying bodies.

TESTS

Comprehensive tests on samples usually are available only in properly equipped laboratories but in recent years some plant operators have acquired the necessary apparatus for sieve tests, tests for organic impurities, clay and silt and, in a few instances, Los Angeles rattler testing machines. No attempt is made herein to describe in detail exact laboratory test methods but reference is made to the more important test methods. Test methods of the American Society for Testing Materials are almost universally accepted as standard.

The value of a deposit may be roughly determined by certain field tests to determine: (1) specific gravity; (2) absorption; (3) organic impurities present; (4) clay and silt; (5) size gradation and fines present; (6) percentage of unsound particles, and (7) the presence of deleterious coatings.

Specific Gravity—An accurate laboratory method for determination of specific gravity and absorption of sand and gravel is described in ASTM Designations C127-42 and C128-42.

Organic Impurities—The presence of organic impurities such as leaves, lignite, and coal is usually determined in the field by the colorimetric test. This test consists of filling a 12-oz graduated clear-glass bottle with a sample of sand to the $4\frac{1}{2}$ -oz mark. A 3 pct solution of sodium hydroxide in water is added until the volume of the sand and liquid indicated after shaking is 7 liquid ounces. The bottle is shaken thoroughly, then allowed to stand for 24 hr. Then the color of the clear liquid above the sand is observed. Clear or light yellow color indicates satisfactory sand for concrete as far as organic impurities are concerned. A strawish color indicates the sand to be suitable only for certain classes of concrete. A dark color would rule out the material unless lignite were present, in which case mortar-strength tests would indicate whether or not there was cause for rejection. See ASTM Designation C40-33 for an accurate method of determining organic impurities.

Clay and Silt—A simple sedimentation test for the quantity of clay and silt present in sand can be made with the aid of a 32-oz graduated bottle. Fill the bottle to the 14-oz level and then with water to the 28-oz level. Then shake thoroughly and allow an hour or more for settling. One ounce of sediment above the sand roughly equals 3 oz of clay and silt.

Size Gradation—A determination of the sieve analysis of the material at hand can be made from a weighed sample of dried material from which the clay and silt have been removed. Passage over a single screen of the proper mesh, which is agitated until refusal (all finer sizes passed), will give a quick determination of the sand percentage. Passage of the sand fraction through testing sieves, preferably ASTM

Standard Nos. 4, 8, 16, 30, 50 and 100-mesh sieves, will give the respective fractions between sieves and the determination will be made by weighing. Similarly, the fractions of gravel between various screen openings can quickly be determined. For ASTM standard procedure, see Designation C136-39.

Unsound Particles—The percentage of soft, friable, and unsound particles present can be determined very roughly by a count of the number of particles separated from a known number of pieces in a gravel sample. However, the sodium sulphate or magnesium sulphate soundness tests require laboratory apparatus, since materials often show no soft particles on visual examination. Standard test procedure for both fine and coarse aggregate is described in ASTM Designation C88-44T.

Abrasion—The Los Angeles abrasion machine is a hollow steel cylinder closed at both ends, with an inside diameter of 28 in. and an inside length of 20 in. There is a steel shelf inside and the machine carries a charge of steel spheres. The test sample consists of 5000 grams of clean, dry aggregate representative of the grading that must pass test. After rotation for 500 revolutions at a speed of 30 to 33 rpm, the material is removed and sieved on a No. 12 sieve and the fraction that is retained is washed, dried, and weighed. The difference between the original weight and the final weight of the test sample is expressed as a percentage of the original weight to indicate the percentage of wear. The standard method of test is described in ASTM Designation C131-44.

MARKETING, USES, AND PRICES

Sand and gravel are generally available over the United States but not all deposits are sufficiently extensive or of high enough quality to warrant commercial operation. Much of the tonnage is too far from consuming centers.

Sand and gravel are low-priced commodities, with plant prices averaging as much as 50 pct less than railroad freight rates charged to haul them, so the commercial industry must depend upon relatively local markets.

Approximately three-fourths of the commercial tonnage of sand and gravel is consumed in building and paving construction. About 15 pct is railroad ballast and the remainder is marketed for fill, filtration purposes, and other miscellaneous uses.

Highway and building construction being the principal markets for sand and gravel, production is markedly affected by trends in those activities. Before World War I and for many years afterward, street and road work had been relatively little in metropolitan areas and emphasis had been shifted to main rural highway construction because

the principal need was for interconnecting main highways. The Federal Aid Highway Act of 1944, providing federal funds for highway and street construction, recognizes that metropolitan areas now need substantial road and street construction to relieve congestion and to handle through highway traffic. Substantial funds have been earmarked for city road and street construction, which will sizably increase the demands for sand and gravel from permanent plants in affected cities. However, highway construction of all classes has been deferred so long that paving sand and gravel will be in great demand over the United

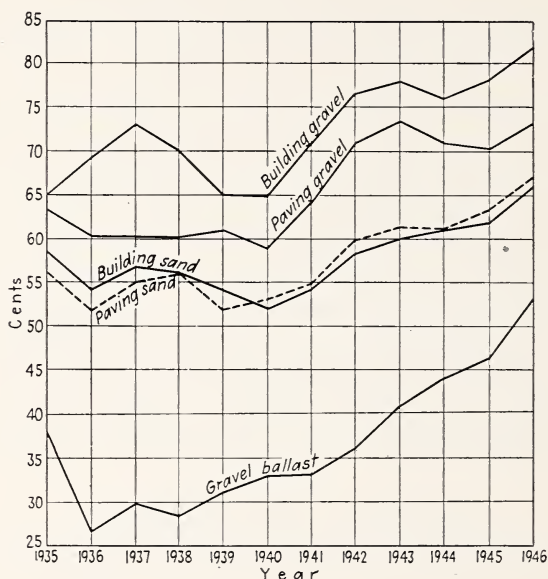


FIG 13—PRICES OF SAND AND GRAVEL.

From Minerals Yearbooks, U. S. Bureau of Mines.

States for many years. Production from noncommercial plants is largely used for secondary roads. That tonnage is also likely to increase, for the Federal Aid Highway Act has allocated substantial funds for rural roads that feed the main highways.

A potential new large-volume market for the industry is in the construction of granular sub-bases for highway construction. Highway engineers have come to realize that highways must have adequate foundations in order to ensure a reasonable life. Properly laid sub-bases of granular materials prevent the rise of capillary water from under the pavement and permit drainage of water away from the slab, thus minimizing the pumping action associated with highways and reducing the likelihood of damage from freezing.

Fig 13 shows graphically the range in prices for sand and gravel since 1935, as taken from the Minerals Yearbooks of the U. S. Bureau of Mines.

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CHAPTER 42

THE SILLIMANITE GROUP*

ANDALUSITE, KYANITE, SILLIMANITE, DUMORTIERITE, TOPAZ

BY FRANK H. RIDDLE† AND WILFRID R. FOSTER‡

GENERAL treatment of the various minerals of importance in refractories appears in the chapter entitled "Refractories" elsewhere in this volume. The present chapter is restricted to a discussion of minerals of the sillimanite group and brings up to date the excellent information contributed by Prof. Paul F. Kerr to the first edition (1937). Since the appearance of that edition, the status of the group has changed somewhat. Kyanite remains the preferred source material for mullite refractories but total consumption of kyanite has increased considerably.⁸⁵ The exigencies of World War II forced an increased dependence on domestic sources and led to an intensification of the search for higher-grade deposits of kyanite and allied minerals. The first discovery of massive kyanite similar to that of India has been reported from Georgia.³⁷ British East Africa has joined India as a substantial supplier of our imported kyanite, but that from India continues to hold preference.⁸⁵ During World War II, prices of both domestic and foreign grades reached peaks unparalleled since the earliest years of the use of kyanite and as yet have shown no tendency to return to prewar levels.

Topaz, by virtue of the deposit outlined in South Carolina, merits inclusion in the group.^{20,36,95} Large andalusite deposits, which threaten to rival our one large domestic occurrence, have been found in Russia.^{69,88} Sillimanite has not yet attained an important position among these useful minerals because of the lack of accessible deposits of high-quality material in adequate supply.^{37,50,58} Tests by the Bureau of Mines have indicated the possibilities of economically beneficiating low-grade sillimanite and kyanite.^{105,106,140} Government, university, and industrial

* Contribution from the Research Laboratories of the Champion Spark Plug Co. Ceramic Division, Detroit, Michigan, prepared with the cooperation of Herbert F. Royal, Director of Research.

† Vice President and Factory Manager, Champion Spark Plug Co., Ceramic Division, Detroit, Michigan.

‡ Petrographer, Champion Spark Plug Co., Ceramic Division, Detroit, Michigan.

laboratories have done much research to adapt our own domestic deposits of this mineral group to the needs of the ceramic industry.^{38,78,79,-80,127,157}

BRIEF HISTORICAL OUTLINE

The presence of "sillimanite" (now known to be mullite) in porcelain and refractories has been known since before the turn of the century.^{73a,153a,155a} Early workers disagreed on its exact composition and some assigned a formula close to that of the later discovered mullite. Fundamental work on the $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ system led workers at the Geophysical Laboratory in Washington to decide that sillimanite is the only stable compound of the system.¹³⁴ This work, although revised in a later study,¹³ served to arouse interest in sillimanite among ceramists.

During World War I, Bureau of Standards investigators were given the problem of developing pyrometer tubes similar to the Marquardt tubes previously imported from Germany.^{48a} A little later they were assigned the task of developing an improved spark-plug porcelain. They reasoned that if the "sillimanite" normally produced in the firing of porcelain is beneficial, an increase in its amount by the addition of either synthetic or natural sillimanite might be more so. Accordingly they increased it at the expense of quartz, adding synthetic sillimanite, since natural material was not available in quantity.^{8,10,111,114} The new type of porcelain showed definite superiority in thermal expansion and mechanical strength.^{112,120} When tried in refractories, it showed excellent load-bearing properties.⁹

This work, first reported in 1918, at once aroused a lively interest in the search for natural sources of sillimanite and its related minerals. As a result of diligent effort, the large andalusite deposits in California were discovered in 1919.⁵⁶ Within the next several years large deposits of sillimanite and kyanite in India²⁸ and kyanite in the United States had been reported.⁴⁶

In 1924, revision of earlier work proved mullite to be the only stable phase in the $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ system.¹³ It also confirmed a growing suspicion among other workers that sillimanite was not the product in attempts to synthesize or thermally dissociate sillimanite or related minerals.²⁵ This new knowledge and the availability of the natural minerals in quantity led to intensive research to utilize them in ceramic products, resulting in a wide variety of uses.

The remoteness of the large deposits of sillimanite in India, and the lack of commercial ore in this country, have caused it to be neglected. Dumortierite soon took its place beside the others with the opening in Nevada of workable deposits, known since 1917 but ignored until about 1925 for want of a commercial use.⁶⁰ Many new deposits of the sillimanite minerals, largely of kyanite, have been discovered or worked during

the past 20 years. Kyanite has been most widely used, because most readily available from both domestic and foreign sources. Discovery of a topaz deposit in South Carolina has aroused interest in the practical use of this mineral.⁹⁵ Throughout the entire period of these developments of the natural minerals, synthetic "sillimanite" (mullite) has continued in favor for certain applications.

COMPOSITION AND STRUCTURE

The sillimanite group includes andalusite, kyanite, and sillimanite, all having the same chemical composition ($\text{Al}_2\text{O}_3\cdot\text{SiO}_2$) but different crystallographic, physical, and optical properties. Two other minerals, because closely allied in composition and thermal behavior, are also included in the group; that is, dumortierite and topaz, with the formulas $8\text{Al}_2\text{O}_3\cdot\text{B}_2\text{O}_3\cdot 6\text{SiO}_2\cdot\text{H}_2\text{O}$ and $\text{Al}_2(\text{F},\text{OH})_2\text{SiO}_4$, respectively. A sixth mineral, mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$), is formed by heating any of the other five to high temperatures: It must also be included, since its properties account for the merits of the group as ceramic raw materials. In the industry, the term "sillimanite" is often loosely used to indicate any of these minerals or their products. The aluminum silicate composition gives chemical stability, important both in industrial use and in natural concentration of the minerals.

All these minerals crystallize in the orthorhombic system except kyanite, which is triclinic. Their internal structures are well understood and fairly complete X-ray data have been presented.^{15,149} Their X-ray patterns, obtained with an X-ray spectrometer, are reproduced in Fig 1. Only sillimanite and mullite show similar patterns due to their very close structural similarity.^{16,89,124} The existence of mullite was long overlooked because of this similarity, reflected also in similar optical properties. Laboratory study of the system $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ (Fig 2) led to the discovery of the compound $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$, and to the proof that it rather than sillimanite is present in porcelain.¹³ It was found in nature in the reexamination of some fused argillaceous sediments earlier described¹⁵¹ from the Isle of Mull, and was therefore named mullite.¹⁴

PHYSICAL AND OPTICAL PROPERTIES

The principal physical and optical properties¹⁵⁹ of the minerals are presented in Table 1. The ordinary physical properties usually suffice to distinguish the individual minerals, except when intimately intergrown with other minerals. Evaluation of such mixtures is often aided by determining the specific gravity,^{56,118} the calcined appearance,³⁵ or the fluorescent response,³⁴ of typical lumps of the ore. The use of gravity separation during microscopic analysis of such ores has been described.³³ Hardness, coupled with chemical stability, leads to the preservation of

placer deposits and residual boulders. Physical properties important in the beneficiation of impure ores are specific gravity, nonmagnetic and dielectric properties, and selective response to wetting agents.

Comparison of the optical properties of sillimanite and mullite makes it clear why the mullite in porcelain was long mistaken for sillimanite. Optical properties are useful in identifying the minerals in ore samples; they also permit rough quantitative analysis of the powdered ores, thus

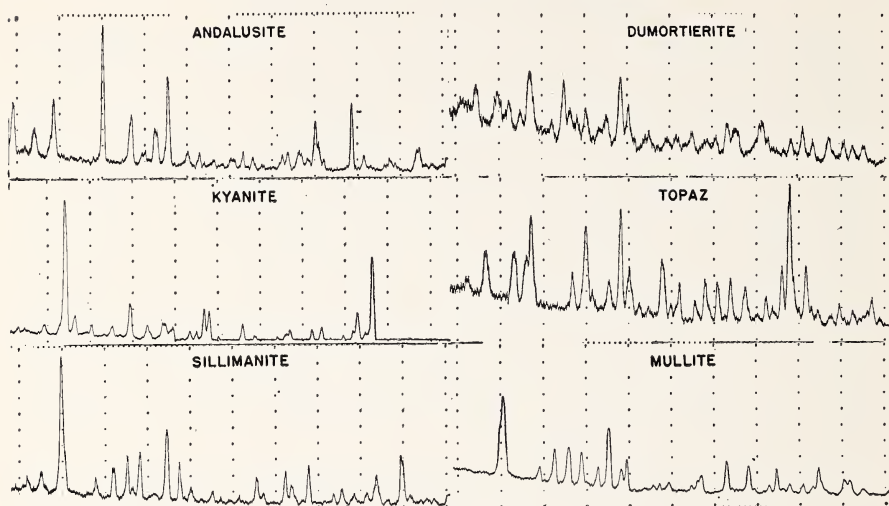


FIG 1—X-RAY SPECTROMETER PATTERNS OF THE SILLIMANITE MINERALS.

Prepared in the Petrographic Laboratories of the Champion Spark Plug Co., Ceramic Division. See also ASTM card file of X-ray Diffraction Data (1945), cards II-446, II-3044, II-1032, II-1460, II-963.

giving rapid checks on the uniformity of successive shipments. Diffraction patterns obtained with an X-ray spectrometer can be used to a like end. In contrast, chemical analysis gives no direct information on the minerals present or their proportions but it gives such useful data as the $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ ratio and the amounts of undesirable iron oxide, titania, and alkalis.

THERMAL PROPERTIES

Many studies have been made of the thermal behavior of the sillimanite minerals.^{13,15,19,41,79,98,102,146,153} The principal results are summarized in Table 1. Behavior on heating is of paramount importance in the industrial use of the minerals. Except for mullite, which is stable up to 1810°C, all are unstable above 1545°C and break down at or below that temperature to yield mullite and free silica, the latter probably as cristobalite. Their role as mullite formers accounts for their value in ceramic products. Mullite imparts to the products such highly desirable properties as high refractoriness, low thermal expansion with resultant

TABLE 1—Physical, Optical, and Thermal Properties

MINERAL		ANDALUSITE	KYANITE	SILLIMANITE	DUMORTIERITE	TOPAZ	MULLITE
CHEMICAL FORMULA		$Al_2O_3 \cdot SiO_2$	$Al_2O_3 \cdot SiO_2$	$Al_2O_3 \cdot SiO_2$	$8Al_2O_3 \cdot 9O_2 \cdot 6SiO_2 \cdot 7H_2O$	$Al_2(F, OH)_2SiO_4$	$3Al_2O_3 \cdot 2SiO_2$
CRYSTAL SYSTEM		ORTHORHOMBIC	TRICLINIC	ORTHORHOMBIC	ORTHORHOMBIC	ORTHORHOMBIC	ORTHORHOMBIC
CLEAVAGE		(110) DISTINCT	(100) PERFECT (001) PARTIAL	(010) PERFECT	(100) DISTINCT	(100) PERFECT	(010) PERFECT
COLOR		GRAY, RED, PINK, GREEN, BROWN	(100) PERFECT: (001) GOOD GRAY, WHITE, GRAY, GREEN, BROWN	WHITE, GRAY, GREEN, BROWN, YELLOW	BLUE, PINK, LAVENDER, GREEN, WHITE	YELLOW, WHITE, GRAY, CLAY, RED, BLUE, BROWN	GRAY, WHITE, PINK
LUSTER		VITREOUS	VITREOUS, PEARLY	VITREOUS, SILKY	VITREOUS, DULL	VITREOUS, GLASSY	VITREOUS
HARDNESS		7.5	8 PARALLEL TO 110° 9 PARALLEL TO 100°	6 TO 7	7	7 TO 8	6 TO 7
SPECIFIC GRAVITY		3.13 TO 3.20	3.53 TO 3.67	3.23 TO 3.24	3.22 TO 3.43	3.4 TO 3.6	3.150 (PURE)
REFRACTIVE INDICES	α	1.629 TO 1.640	1.712 TO 1.717	1.687 TO 1.693	1.689 TO 1.678	1.607 TO 1.629	1.636 TO 1.653
	β	1.633 TO 1.644	1.720 TO 1.722	1.658 TO 1.670	1.684 TO 1.691	1.610 TO 1.631	1.642 TO —
	γ	1.639 TO 1.647	1.728 TO 1.729	1.677 TO 1.684	1.686 TO 1.692	1.617 TO 1.636	1.653 TO 1.662
OPTICAL CHARACTER		BIAxIAL NEGATIVE	BIAxIAL NEGATIVE	BIAxIAL POSITIVE	BIAxIAL NEGATIVE	BIAxIAL POSITIVE	BIAxIAL POSITIVE
OPTIC ANGLE		$2V = 65^\circ$	$2V = 62^\circ$	$2V = 20^\circ$ TO 30°	$2V = 30^\circ$ TO 52°	$2V = 40^\circ$ TO 65°	$2V = 45^\circ$ TO 50°
DISPERSION		$r > v$ FAINT	$r > v$ WEAK	$r > v$ STRONG	$r < v$ STRONG	$r > v$ DISTINCT	$r > v$ STRONGER THAN SILLIMANITE
ORIENTATION		$I = c; Z = a$	I ALMOST \perp TO $AC = 30^\circ$	$I = c; Z = c$	$I = c; Z = a$	$I = c; Z = c$	$I = a; Z = c$
PLEOCHOISM		ABSENT TO STRONG	ABSENT TO WEAK	ABSENT TO WEAK	STRONG	ABSENT TO WEAK	ABSENT TO STRONG (ARTIFICIAL NATURAL)
SHAPE (POWDERS)		IRREGULAR GRAINS	ALMOST RECT. LATES	NEEDLES OR LATES	NEEDLES OR LATES	IRREGULAR GRAINS	NEEDLES OR LATES
ELONGATION		NEGATIVE, IF SHOWN	POSITIVE	POSITIVE	NEGATIVE	UNCERTAIN IN POWDER	POSITIVE
EXTINCTION		PARALLEL, IF SHOWN	INCLINED UP TO 30°	PARALLEL	PARALLEL	UNCERTAIN IN POWDER	PARALLEL
DECOMP. TEMP.		1350° TO $1450^\circ C$	1100° TO $1400^\circ C$	1650° TO $1650^\circ C$	$< 1000^\circ$ TO $1250^\circ C$	$< 1000^\circ$ TO $1400^\circ C$	STABLE TO $1810^\circ C$
VOLUME CHANGE		VERY SLIGHT INCREASE	NOTABLE INCREASE	SLIGHT INCREASE	SLIGHT INCREASE	SLIGHT INCREASE	LOW COEFF. OF EXPANS.
DENSITY CHANGE		3.04 AT $1445^\circ C$	3.03 AT $1445^\circ C$	3.10 AT $1445^\circ C$	2.89 AT $1445^\circ C$	3.02 AT $1200^\circ C$	—
MICROSTRUCTURE		PARALLEL MULLITE-SILICA AGGREGATES	MULLITE NEEDLES \perp GRAIN—BORDERS	PARALLEL MULLITE—MULLITE AGGREGATES	INTERFERING FAN-SHAPED AGGREGATES	INTERFERING FAN-SHAPED AGGREGATES	DEPENDS ON PARENT MINERAL
$Al_2O_3:SiO_2$ RATIO		1.72	1.72	1.72	2.25	2.33 TO 2.46	2.65
η LIQUID AT $1545^\circ C$		14	14	14	4	3	0
THERMAL PROP.							

resistance to heat-shock, intermediate thermal conductivity, high load-bearing ability even at high temperatures, and resistance to chemical corrosion, particularly by acid slags.

The various minerals though similar in their decomposition products, differ in the temperatures required for both incipient and rapid decomposition, in microstructures, in volume and density changes, and in the relative proportions of mullite and silica. These factors have a bearing on the choice of mineral and the preparatory treatment, if any, it receives.

There is no fixed decomposition temperature for any of the group and the rate of breakdown for a given mineral varies with grain size, time, and temperature.^{5,15,41,122} The ranges given in Table 1 extend roughly from the temperature of earliest breakdown to that considered adequate in commercial practice. Topaz and dumortierite are the most readily dissociated, followed in order by kyanite, andalusite, and sillimanite. In practice, andalusite has an advantage in that mullitization is gradual and progressive at commercially attained temperatures. Sillimanite is scarcely affected at such temperatures, whereas the others are too readily decomposed.^{16,122}

The volume changes on calcination affect the use of the minerals. All show a decrease in density, hence an increase in volume, on calcination. For all except kyanite, the change is so slight that they are essentially volume-constant and can be used without precalcining. Kyanite undergoes a notable expansion. It is, therefore, usually calcined before use, although in some cases raw kyanite in low percentages has been tried with success. Because of the expulsion of the bulk of their volatiles, dumortierite and topaz undergo weight losses of up to 6.6 pct¹⁵ and 16 to 21 pct,^{79,102,146} respectively. Despite this, they are practically volume-constant. For topaz, precalcination to eliminate fluorine is considered necessary, and is attended by difficulties.^{20,102} Once completely mullitized, no further volume change occurs in any of the minerals, aside from the normal thermal expansion, except coarse-bladed kyanite. Recent work by Booze has given further information regarding the volume constancy of topaz on calcining at 3000°F. He states that continued heating at 3000°F reveals a very considerable residual shrinkage. In his opinion, a calcining temperature in excess of 3100°F would be necessary to render topaz suitable for refractory use.¹⁶⁵

The calcined microstructure of the minerals varies somewhat. Kyanite, dumortierite, and topaz give an interlacing aggregate of mullite needles, said to promote mechanical strength. Andalusite and sillimanite show a parallel orientation of mullite crystals. Kyanite, on account of its expansion, gives a highly porous product. On the basis of the density decrease, this expansion should be about 16 pct but because of cracking and exfoliation it amounts to as much as 200 pct.⁷⁹ This is particularly

true of the coarse, bladed domestic kyanite, which consequently has a high shrinkage and is difficult to bond in use. In contrast to the soft, friable grog of this type of kyanite, massive India kyanite yields a hard, tough grog of considerably lower porosity.⁷⁹ The small amount of fluorine remaining in calcined topaz may have a beneficial mineralizing action in use.¹⁰² The boric oxide released into dumortierite-bearing refractories on firing is believed to have similar merit.¹¹⁸

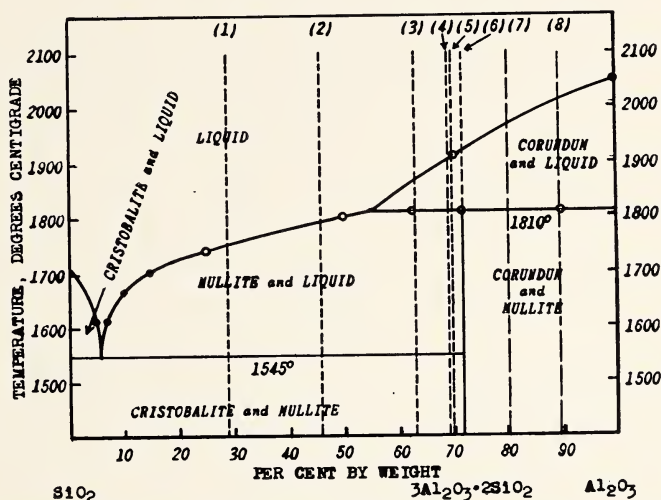


FIG 2—EQUILIBRIUM DIAGRAM OF SYSTEM $\text{Al}_2\text{O}_3\text{-SiO}_2$, AFTER BOWEN AND GREIG¹³ WITH ADDED COMPOSITION LINES.

- | | |
|------------------------------------|---------------------------------------|
| 1. Dehydrated pyrophyllite. | 5. Devolatilized topaz. |
| 2. Dehydrated kaolin. | 6. Mullite. |
| 3. Andalusite-kyanite-sillimanite. | 7. Dehydrated Missouri diaspore clay. |
| 4. Devolatilized dumortierite. | 8. Dehydrated typical bauxite. |

The modified $\text{Al}_2\text{O}_3\text{-SiO}_2$ diagram shown in Fig 2 is useful in evaluating the refractoriness of aluminum silicate minerals and mixtures. The superiority of andalusite, kyanite, or sillimanite over kaolinite or pyrophyllite is clear from a comparison of the relative amounts of siliceous liquid formed at or about 1545°C. Dumortierite and topaz have the advantage that their $\text{Al}_2\text{O}_3\text{-SiO}_2$ ratio more closely approaches that of mullite, which gives no liquid up to 1810°C. The still greater refractoriness of such aluminous mixtures as electrocast mullite-corundum, calcined diaspore-clay or bauxite, and andalusite-diaspore mixtures is also apparent.

Certain other properties that are either strictly thermal or related to their use at high temperatures are highly significant in practical applica-

tion. Electrical resistivity tests indicate that kyanite, sillimanite, and andalusite stand in that order as regards merit in this property.⁶⁶ Pertinent comparative data show the relative merits of mullite and other types of insulating materials as regards thermal expansion, resistivity, and thermal conductivity.¹¹⁹

A trade bulletin gives comprehensive information on these and other properties for all of the usual heavy-duty refractories. The data covering the aluminum silicates, taken therefrom, have been incorporated in Tables 2 and 3.⁹¹

TABLE 2—*Comparative Properties of Commercial Aluminum Silicate Refractories*⁹¹

Properties	Very High	High	Medium	Low	Very Low
Refractoriness.....	M	MSK	F		
Load bearing at high temperatures...		SK		F	
Spalling resistance.....		SKF		M	
Heat-transfer characteristics.....	MSKF		MSK	F	
Resistance to oxidation.....					
Resistance to reducing atmospheres..		MSKF			
Acid-slag resistance.....	MSKF				
Basic-slag resistance.....			MSK	F	
Resistance to slag adherence.....				MSKF	
Resistance to slag penetration.....	M	SKF			
Elec. resistance at high temperatures.		MSK	F		
Weight of refractory article.....		M	SKF		
Resistance to mechanical abrasion....	M	SK	F		

M. Mullite (fused or cast).

S. Sillimanite, andalusite, kyanite.

K. Kaolin.

F. Fire clay.

TABLE 3—*Properties of Typical Mullite Refractories*

Properties	Temperature	Data for Mullite Brick
Composition.....		Al ₂ O ₃ : 62%; SiO ₂ : 38%
Pyrometric-cone equivalent.....		Cone 38
True specific gravity.....		3.03
Approximate weight, 9-in brick.....		8½ lb
Linear coefficient of expansion.....	20°–1320°C	45 × 10 ⁻⁷ per deg C
Thermal conductivity.....	95°–1430°C	8.5 Btu/hr/sq ft/in./deg F
Mean specific heat, cgs.....	20°–800°C	0.175
Deformation under load.....	At 1450°C	0% (50 psi)
	At 1650°C	2.0% (50 psi)
Constancy of volume.....	Up to 1650°C	No appreciable change

ORIGIN

The origin of mullite, both in nature and in ceramic practice, is well understood, and its stability relations have been completely worked out.¹³ A low-temperature form of mullite is claimed to exist.⁵² Attempts to syn-

thesize andalusite, kyanite, and sillimanite at atmospheric pressure have failed. Andalusite is reported to have formed in a bomb at 350° to 450°C .⁴⁵ Sillimanite has been produced at 3000 psi pressure and at a temperature between 800° and 900°C .⁸⁶ Artificial kyanite has never been prepared.⁴⁵ The synthesis of topaz has been reported¹²⁹ and that of dumortierite has been claimed.¹⁶³

Although there is some field evidence on the physicochemical conditions of their formation, all attempts to effect interconversions between andalusite, kyanite, and sillimanite in the laboratory have failed. Their stability relations, therefore, are somewhat obscure. There is general agreement that they require rather high temperatures (geologically, not industrially, speaking) and considerable pressures for their formation. The deposit of andalusite of White Mountain, California, is believed to have formed at a depth of at least 8,000 to 10,000 ft and at a temperature of about 500° to 600°C .⁷² There is reason to believe that sillimanite forms at higher temperatures than kyanite^{37,45,141} and andalusite. That kyanite should develop above and sillimanite below 1320° to 1380°C ⁴² is highly questionable, and the temperatures are excessive. Higher pressure is believed necessary for sillimanite than for andalusite.⁴² A plausible theory is that andalusite and kyanite are metastable forms, monotropic toward the stable sillimanite and that kyanite is favored over andalusite by shearing stress.⁴⁵ However, it is not certain that great pressure would not proxy for stress in causing the formation of kyanite, and the occurrence of kyanite in quartz veins and pegmatites makes it questionable whether either excessive pressure or shearing stress is required.

Considerable controversy exists as to the roles played in the genesis of andalusite, kyanite, and sillimanite by regional and thermal metamorphism, hydrothermal action, aluminous composition of intrusive and wall rock, and assimilation. All three minerals appear to have essentially the same mode of origin, except for slight differences in pressure and temperature conditions.^{29,37} They occur almost invariably in metamorphic terrains. Evidence of pneumatolytic activity is strong in many cases^{63,65,145} but this does not prove the source or mode of origin of the aluminum silicates.²⁹ Many incline to the belief that they form from highly aluminous beds of xenoliths either by mere metamorphism (regional or thermal) or through sorting action of magmatic solutions, but without introduction of material from the latter.^{28,29,37,59,63,72,156} Others believe that the aluminous material originates largely or wholly in the magma or its residues.^{47,59,74,144,145} Further careful study may resolve such differences of opinion. The composition and field relations of topaz and dumortierite leave little doubt of a pneumatolytic origin. Here again, however, it might be argued whether the requisite alumina came from the magma or the wall rock.

MODE OF OCCURRENCE

Andalusite—Andalusite is characteristically found in argillaceous slates and schists produced by contact-metamorphic action of granitic intrusives. Dioritic and more basic intrusives also may cause its formation. It is sometimes found within granite bodies, especially those of the two-mica variety. Mica schists and gneisses also may harbor it. It occurs as lenses and pockets in pegmatites and quartz masses and as replacement bodies produced by pneumatolytic action of residual magmatic solutions. It is not a typical product of regional metamorphism. It commonly occurs as long, prismatic crystals of nearly square cross section. Even in slates and schists, it sometimes grows to large size. The chiastolite variety featuring carbonaceous impurity arranged in a cross is typical of impure slates and schists. Large crystals are usual in pegmatites and lenses in quartz and coarse, columnar crystal groups are not uncommon. A massive, granular, anhedral structure is also sometimes shown. Common associates are quartz, muscovite, pyrophyllite, diaspore, topaz, garnet, biotite, tourmaline, lazulite, rutile, dumortierite, and sometimes sillimanite and kyanite.

Kyanite—Kyanite occurs as disseminated crystals in schists, quartzites, or gneisses produced by regional metamorphism. Later contact metamorphism of such rocks by igneous intrusives, with accompanying hydrothermal effects, probably accounts for the coarsely crystallized and massive segregations in these rocks, and also for the pockets and lenses in pegmatites, quartz veins and quartzose masses. Veinlets composed almost entirely of kyanite are also known. It typically forms long-bladed crystals, often of large size, or coarse interlocking bladed or radiating fibrous aggregates. Much less common is the massive variety, featuring randomly oriented and interlocking small-crystal aggregates, the latter varying in size from small buttons to huge boulderlike nodules. The minerals most commonly accompanying kyanite are quartz, muscovite, biotite, feldspar, garnet, rutile, staurolite, tourmaline, corundum, topaz, lazulite, and sometimes andalusite, dumortierite, and sillimanite.

Sillimanite—Sillimanite is of widespread occurrence in belts of sediments that have been subjected to either regional or contact metamorphism or both. It is found, therefore, in quartz and mica schists, gneisses, slates, and hornfels. It occurs, though rarely, within granitic rocks of the two-mica type. It is not unknown in pegmatites but appears to be less common than andalusite and kyanite. It frequently occurs in stringers, nodules, and lenses near the pegmatites. When disseminated through schists, it develops as isolated, long, prismatic crystals, usually as the finely fibrous fibrolite variety, or as coarse bundles of crystals. The nodular massive form features fibrolite needles or coarser prisms densely packed in interlocking subparallel or radiating bundles. Quartz,

muscovite, biotite, cordierite, corundum, garnet, rutile, and occasionally andalusite, dumortierite, and kyanite, are the more usual associates.

Dumortierite—Dumortierite is most commonly found in pegmatites that cut aluminous rocks, such as sericite schists and cordierite or corundum gneisses. Apparently it is related to hydrothermal effects produced by igneous intrusions upon such rocks. It has been reported within granite masses as an accessory mineral. It occurs as replacement bodies, sometimes of large size, formed within or in close proximity to highly aluminous rocks. It appears to be strictly a pneumatolytic or pegmatitic mineral rather than one due to mere pressure or temperature metamorphism. Quartz masses and veins sometimes contain it, or it may form veins and fissure fillings of almost pure dumortierite. It may occur as isolated euhedral prismatic crystals of fair size but more usually exhibits fibrous aggregates of fine, acicular needles. In the massive variety, it forms great matted masses of such fine needles. Minerals such as muscovite, quartz, feldspar, cordierite, andalusite, sillimanite, kyanite, corundum, diaspore, pyrophyllite, topaz, fluorite, tourmaline, and rutile may accompany it.

Topaz—Like dumortierite, topaz is characteristically a pneumatolytic mineral formed during the final stages of consolidation of granitic magmas. It is thus found in veins and cavities in granites and rhyolites, or in veins or pegmatites in the contact zones of the surrounding schists and gneisses. In the largest known occurrence, topaz occurs in a gold-bearing quartz lode that has replaced a rhyolitic breccia. It usually forms stout, prismatic crystals truncated at one end by pyramidal faces. The massive form, which occurs in the replacement body just mentioned, is very fine grained, and microscopically exhibits the mosaic texture shown by chert. Commonly associated minerals include quartz, feldspar, muscovite, beryl, tourmaline, cassiterite, fluorite, dumortierite, andalusite, and pyrite.

Mullite—Mullite is of rare natural occurrence, because rather unusual conditions are required for its formation. When basaltic igneous magmas, the hottest in nature, invade highly aluminous rocks, inclusions of the latter are sometimes engulfed and partially fused, minute criss-cross needles of mullite crystallizing during cooling. Such fused argillaceous sediments, termed buchites, are found in the Western Isles of Scotland (including the type locality, the Isle of Mull) and other areas where similar conditions prevailed.

DISTRIBUTION OF DEPOSITS

Andalusite

In 1917, an andalusite deposit was reported in the Inyo Mountains of California but excessive quartz made it useless commercially.⁶⁷ Two years later, large high-grade deposits were found 2 miles farther east.

These deposits have been almost the sole source of andalusite in this country. They are at White Mountain, near Mocalno, Mono County, California, at an elevation of 7000 to 9000 ft, in a zone roughly 2 miles long and 30 ft wide.^{57,63,72,97} The ore of the upper workings occurs as irregular lenses in a quartz mass bordered on each side by sericite schist. It averages 75 to 85 pct andalusite. More accessible deposits, in which diaspore rather than quartz is the chief associate, were later located and exploited lower down on the slope. Extensive areas of andalusite schists have been reported near Berrenda, Madera County.⁸¹

Near Oreana, Nevada, irregular lenses of andalusite large enough to be of possible economic value occur in the dumortierite deposits.⁶⁵ Andalusite is associated with mica, quartz, corundum, diaspore, and sillimanite near Hawthorne, Nevada.⁵⁸ It forms a vertical veinlike deposit 2 to 4 ft thick, about 3000 ft long and at least 100 ft deep. The Bureau of Mines believes that the workable reserves in this area may be very large.¹⁷⁵

There are small irregular occurrences of andalusite in a belt of pegmatites near Summit Peak in the Black Hills of South Dakota.²⁴ It occurs in graphitic schists and pegmatites in the tin and tungsten deposits of Silver Hill, Washington.⁹⁴ Minor occurrences are noted in a number of pegmatites in California.^{74,87,156} Large quantities occur in lenses or coarse crystals in quartz mica schist on Oak Hill, near Littleton, Massachusetts.⁵⁵ Andalusite is reported in the pegmatites of the Jardine district, Montana.¹⁶⁹ Andalusite ore from Larimer County, Colorado, is very high grade (at least 80 pct), although it is partially altered to sericite, and the amount available is not known.

Large and rich deposits of andalusite have been discovered in Kazakhstan, Russia, which may surpass the White Mountain, California, occurrence.^{69,88} Fourteen separate deposits occur mainly as pockets in quartzite. Andalusite content varies from 10 to 80 pct and the reserves run into the millions of tons. At Silvretta, Switzerland, it occurs with kyanite.¹⁴³ Deposits are known to occur in Spain, and samples shipped from Pontevedra, but unknown as to exact source, contained 75 pct andalusite, though containing considerable biotite and tourmaline.

Sands containing as high as 90 pct andalusite occur in the Zeerust and Marico districts of western Transvaal in Africa.⁹⁶ They are said to compare favorably with domestic material, but andalusite sands from the Gold Coast of Africa are too high in iron and alkalis.⁸⁵ Boulderlike outcrops of massive andalusite are described from South Australia.⁵⁴ Occurrences have also been noted in Western Australia, where large masses of pure pegmatite andalusite up to 50 lb in weight occur in the Ninghanboun Hills.^{135,136} Andalusite has been reported in India but not in commercial deposits.¹³³ An excellent grade of andalusite, said to be from Korea, has recently been received in this country. It is coarsely

crystallized and pink in color and, with the exception of small amounts of muscovite and kyanite, is practically free of impurities. It is said to occur in crystalline schists and gneisses and in quartz veins. Considerable information on foreign occurrences of andalusite and of the other sillimanite minerals is contained in a recent French report.^{73d}

Kyanite

The most important known deposits of kyanite in the United States are in the Piedmont belt of crystalline schists, extending from Virginia to Alabama. In Virginia, the chief deposits are in the central part of the state.^{59,103} One of the largest in size and output in the entire country is at Baker Mountain, near Pamplin, and a large undeveloped deposit is at Willis Mountain, 40 miles to the northeast. In both deposits, the kyanite occurs in quartzite and schist and averages 20 to 30 pct.^{49,58,126} Minor occurrences outside of the central productive area of the state have been reported in schists, pegmatites, and gold-bearing veins.⁵⁹

Commercial deposits of kyanite occur in North Carolina.^{31,39} The Black Mountain range contains numerous bands of kyanite-bearing gneiss. The most important deposit is on Celo Mountain, near Burnsville, where a huge lens 2000 ft long and 300 ft wide has been worked until recently.^{75,76} Several million tons of disseminated ore averaging 11 pct kyanite and 8 pct garnet are available here.⁷⁹ In South Carolina, some kyanite has been produced at Henry Knob, York County, and resumption of activity here is planned.¹⁷⁶

Extensive deposits occur in Georgia, the most important being in a U-shaped belt 30 miles long in Habersham and Rabun Counties, north of Clarkesville.^{37,103,142} These deposits are the disseminated type averaging 6 to 8 pct in schist, or placer deposits derived from the schist. Veins and lenses of coarse kyanite also occur, sometimes as residual boulders or "dornicks." In Towns County, kyanite lenses have been worked on Gumlog Mountain. Occurrences of massive kyanite closely resembling that imported from India have been found as lumps and boulders in Cherokee, Pickens, Dawson, and Gilmer Counties. The available tonnage at any one locality is not large but further search may disclose commercial quantities. A large and rich kyanite deposit occurs at Graves Mountain, Lincoln County, where it constitutes about 30 pct of the quartzite.¹⁵⁵ Residual blocks of high-grade coarse-bladed kyanite are known from five counties of Alabama. The vein source of these blocks is in Turkey Heaven Mountain, near Heflin, Cleburne County.¹⁷ A rather extensive commercial deposit occurs at the foot of the Cargo Muchacho Mountains near Ogilby, California.¹²⁵ The kyanite occurs in schists and gneisses in a matrix of quartz, and makes up 25 pct of the rocks. Large deposits are known in Wyoming, especially in the Encampment district, and those in the vicinity of Wheatland are said to be of commercial impor-

tance.^{46,100} In Iron County, Wisconsin, kyanite of good quality constitutes 8 to 10 pct of gneissic rocks.⁸⁵ Occurrences have also been noted in Tennessee near Mount Pleasant,⁸⁵ in Maryland,⁶⁸ in Arizona north of Yuma, in Massachusetts at Chesterfield, in Pennsylvania at Darby, in Rio Arriba and Taos Counties, New Mexico, and in southern Idaho.¹⁰⁰ Kyanite of possible commercial interest occurs in schists, gneisses, and pegmatites near Ennis, Montana.¹⁶⁹ Kyanite is an appreciable constituent of Florida beach sands, amounting to 12 to 45 pct near Pensacola.⁸⁴ Massive slide boulders of kyanite have been found near Revelstoke, British Columbia.¹⁰⁹ Their source, when found, may prove to be a commercial deposit.

The chief commercial kyanite deposits in the world occur at Lapsa Buru, Singhbhum district in Kharsawan state, about 100 miles west of Calcutta, India. Segregations of massive kyanite averaging 10 pct of corundum are found in quartz-kyanite rock associated with mica and hornblende schists. Fibrous and coarse-crystal kyanite is subordinate. At least 210,000 tons is available and there may be 10 times this amount.²⁸ Other Indian occurrences are reported in the Bhandara²² and Mysore⁷¹ districts.

In British East Africa commercial deposits of kyanite occur in the territories of Kenya, Nyasaland, and Uganda. Some of these have recently been brought into production.^{3,21,104} In Western Australia occurrences have been described at Smithfield and Clackline,^{83,137,138} and in South Australia near Williamstown.¹ Some of these Australian localities feature massive kyanite in commercial quantities but samples of the ore received in this country show it to be too impure for general use.¹⁶⁶

In the Kola peninsula of Russia, rich kyanite deposits of high estimated reserves are found in quartzose rocks.^{11,43} Lenticular deposits are reported in the schists of Mount Chisovara, in Karelia, Russia.¹² Large reserves of kyanite occur in gneisses and schists in the province of Styria, Austria.²⁷

Sillimanite

No domestic deposits of sillimanite have ever been worked on a commercial scale. The most promising occurrences appear to be those of the southeastern states, particularly North and South Carolina and Georgia.¹⁵⁰ Here sillimanite, like kyanite, occurs as disseminations in the zone of schistose rocks extending along the Piedmont belt. In North Carolina, four major zones of possible commercial ore occur, the sillimanite being associated with mica schists, quartzites, and pegmatites.⁵³ A belt of sillimanite-rich schists has been mapped in Hart, Elbert, and Madison Counties, Georgia. The sillimanite is largely of the coarse prismatic rather than the fibrous type that occurs in deposits on Davy Mountain, on the Georgia-North Carolina line.^{37,50,150} In South Carolina

promising sillimanite deposits occur in quartz mica schists, which form roof pendants over granitic intrusions, in Greenville, Spartansburg, and Anderson Counties.^{37,141,150} It is also reported in the mica schists of Randolph and Clay Counties, Alabama, but the extent and richness are as yet unknown.¹⁵⁰

Quite promising coarse prismatic sillimanite occurs in five areas of a 10-mile belt in southern New Hampshire.⁷ Less promising occurrences are known in other parts of the state.⁴ Sillimanite associated with a good deal of quartz occurs near Custer, South Dakota, and small amounts have been shipped.²⁴ An extensive low-grade deposit that may be amenable to beneficiation is reported in the schists and gneisses near Troy, Idaho.³² High-grade sillimanite rock of possible commercial interest occurs in a zone of gneisses and schists on Currant Creek, on the Canyon City-Guffey road, Colorado.¹⁶⁹ Sillimanite also occurs to a minor extent in veins west of Golden, Colorado, and in various other localities in the state.

Promising occurrences of sillimanite schist are found in quartzite along the Arroyo Hondo in Taos and Arriba Counties, New Mexico.^{62,85} It occurs in schists and pegmatites at Silver Hill, Washington.⁹⁴ At least six of the counties of California are known to have sillimanite-bearing schists but known deposits are too small to be of value.⁵⁶ A large deposit of sillimanite schist occurs in the Funeral Range, 18 miles south of Beatty, Nevada, but it contains considerable included magnetite, and the location is remote.¹⁶⁸

Large deposits of massive sillimanite occur in sillimanite-quartz schists interbedded with cordierite gneiss at Khasi Hills, Assam, India. There are 13 different deposits in a 3-mile by 1-mile belt, but they are very inaccessible. At Pipra in Rewa, India, local segregations of corundum-sillimanite occur in sillimanite schists. This ore must be transported 120 miles by oxcart and truck. The estimated minimum reserves for the two localities is 182,600 tons.²⁸ Smaller and less important occurrences of corundum and sillimanite are known in the Bhandara district.^{22,100}

Sillimanite is an appreciable constituent of beach sands at Travancore, India, and can readily be concentrated by mechanical means.¹³⁹ In the Ninghanboun Hills of Western Australia, dense bundles of sillimanite occurs in granular quartz and quartzite.¹³⁵ Commercial deposits are known also near Clackline, where small lenses constitute about 5 pct of a clay.¹³⁷ It has been reported in Southern Australia also.^{1,54,77} A massive sillimanite deposit in the Broken Hill district of New South Wales has been investigated but shipments to several firms in the United States indicate that it is useless as a substitute for India kyanite.³⁷ Sillimanite occurs with corundum in the norite of the Bushveld igneous complex near Lydenburg, South Africa.⁴⁴ It has been reported also in a metamorphosed bauxite in Namaqualand.²³ Massive sillimanite from Africa is too impure to be of value in refractories.¹⁶⁶

Dumortierite

The only known commercial deposit of dumortierite in the world is near Oreana, Pershing County, Nevada. The ore occurs as lenticular segregations in two parallel zones between quartz-sericite schist.^{60,65,99} Boulders of dumortierite occur about 25 miles from Ogilby, in Imperial County, California, and in nearby Yuma County, Arizona.^{125,160} An interesting occurrence in situ is that near Quartzsite, Arizona, where andalusite, kyanite, sillimanite, and dumortierite are all closely associated.¹⁵⁸ Minor occurrences have been recorded from many other localities, both domestic and foreign.^{60,128} Recently it has been found near Vallenar, Province of Atacama, Chile.¹⁷⁰

Topaz

A large deposit of fine-grained topaz forms part of the gold-bearing lode at the Brewer mine, near Jefferson, South Carolina.^{20,36,95} Its exposed area measures about 25 by 50 ft but the existence of "float" on the slope above the outcrop indicates a greater extent of the body. This is the only topaz deposit of promising size in this country. Samples of excellent topaz have been received from Gunnison County, Colorado, but no data as to its abundance are at hand. Topaz is one of the minor associates of andalusite in the deposits of White Mountain, California.⁷² Although prominent in some specimens, it does not occur in minable quantity, so far as is known. Topaz lumps are sometimes received in shipments of India kyanite.⁷⁹ Brazilian topaz has been tested for its possibilities as a refractory material,^{2,6} so it is assumed that a fair amount must be available. Many topaz localities are known throughout the world but with the exception of those mentioned above, they appear to lack economic possibilities.

POLITICAL AND COMMERCIAL CONTROL

Most domestic production of the sillimanite minerals has been in the hands of private companies, which preferred to own and operate deposits to ensure uniform grade and steady supply. The output from such deposits has never reached the open market until fabrication. Very little of this type of operation is going on at the present time. Mining activity at the andalusite and dumortierite properties of Champion Sillimanite Inc., has been curtailed because of the trend toward pure alumina spark-plug insulators, although andalusite is still heavily relied upon by the parent company for its refractories. The Aluminum Silicates Co. of Los Angeles, has taken over the Ogilby kyanite deposits formerly owned by the Vitrefrax Corporation but does not appear to be yet in production. No recent activity is reported at the Hawthorne, Nevada, andalusite mine formerly worked by the Tillotson Clay Products Co., of Los Angeles. The A. P. Green Fire Brick Co., of Mexico,

Missouri, has been mining a kyanite deposit near Clarkesville, Georgia, for its own use, and has recently prospected some Georgia sillimanite deposits.

A few mining companies have catered to the general trade. Change of ownership is more frequent in such operations. The kyanite deposits of Baker Mountain, near Pamplin, Virginia, pioneered by the McLanahan-Watkins Co., then worked by Phosphate Recovery Corporation and its associate, Kyanite Products Corporation, is now being worked by Kyanite Mining Corporation, which plans also to develop its Willis Mountain property. Mas-Celo mines, which succeeded the pioneer Celo mines at Burnsville, North Carolina, in 1941, was reorganized in 1943 as Yancey Cyanite Co., only to suspend activity early the next year. Two other companies that until recently have been active in Georgia are Georgia-Carolina Minerals Corporation and its successor, Southern Mining and Milling Co. A number of other firms and individuals have mined kyanite sporadically in the southeastern states during the past 10 years. The production of South Carolina topaz is in the hands of United Feldspar and Minerals Corporation, Spruce Pine, North Carolina, and Carolina Mining and Exploration Corporation, Naples, North Carolina.

The bulk of the India kyanite produced is mined by the Indian Copper Corporation and Eastern Minerals Corporation of Calcutta, India.¹⁶⁷ It is impossible to predict the effect, if any, that Indian independence will have on continued production and supply. India also controls the greatest potential supplies of sillimanite. Our own kyanite resources are being augmented by increasing supplies from British East Africa. Australia also controls large potential reserves of kyanite and sillimanite, which doubtless would be available to us. Russia apparently has large reserves of andalusite and kyanite but these probably will be unavailable for export for some time.

PRODUCTION AND CONSUMPTION

The only important current production of any of the sillimanite minerals in this country is that of kyanite by the Kyanite Mining Corporation, Cullen, Virginia. Present output from Virginia is estimated at 15,000 tons yearly.¹⁶⁶ No known current production is taking place in California, although at one time the Vitrefrax Corporation was said to be producing as much as 5000 tons of kyanite per year from its Ogilby deposit, for its own use. Champion Sillimanite, Inc., is inactive at the present time but it has produced, for use by its parent company, more than 20,000 tons of andalusite since 1922, and more than 5000 tons of dumortierite since 1925, at its mines in California and Nevada.

World War II greatly affected production, imports, and consumption of kyanite in this country. Domestic output was greatly stimulated because of uncertainty of supplies from India. Manpower and equipment

shortages and transportation difficulties hampered full production and distribution. Despite threats of a Japanese invasion of India, shortage of shipping space and losses at sea, imports of India kyanite were received quite steadily through the war. The importance of kyanite to our war effort is reflected by the Government's stock-piling and conservation orders relative to India kyanite. Because of this wise policy, our reserves of India kyanite grew so that WPB Conservation Order M-143, effective May 6, 1942, could be withdrawn on Nov. 22, 1943. The stock-pile objective of 5739 tons was reached in February 1944.⁸⁵

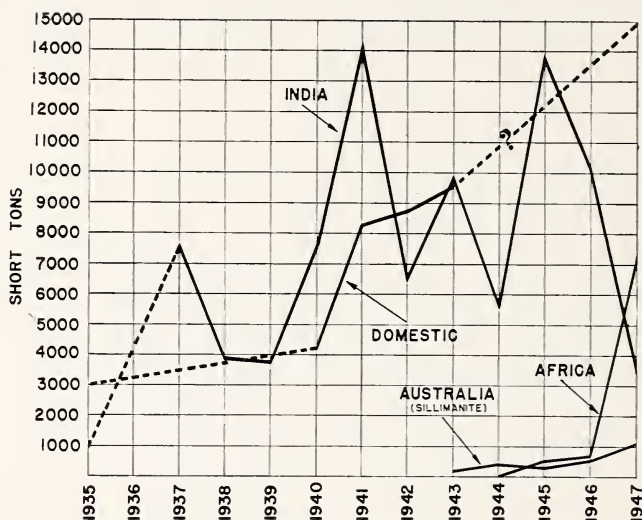


FIG 3—PRODUCTION AND IMPORTS OF KYANITE, UNITED STATES.

The trend in production and imports of kyanite in the United States is shown graphically in Fig 3, prepared from available incomplete data.⁸⁵ In 1935, domestic production was estimated to be at least 3000 tons, and possibly twice that amount. A substantial increase was noted in 1936. Actual production figures were not assembled until 1940. Since 1943, no figures have been released on domestic production, but, judging from the foregoing estimate, there has been a notable increase in the past several years. Domestic production reached an all-time high in 1946.⁸⁵ Imports of India kyanite in 1935 are estimated at somewhat over 1000 tons, and showed an increase in 1936. The all-time high for imports was the 14,285 tons received in 1941. Since that year, imports have dropped off considerably, largely because of difficulties connected with the war. By 1945, conditions had so improved that 13,994 tons was imported. Transportation difficulties and unrest in India, have again adversely affected supplies, so that our imports for 1947 have dropped off to 3792 tons.¹⁷³

Massive kyanite has been mined for more than 20 years in the state

of Kharsawan, India. From 1925 to 1933, inclusive, production totaled 33,000 tons. More recent production has been at the rate of 10,000 to 40,000 tons per year.¹⁶⁶ Shipments of kyanite from Kenya, Africa, are now being made at the rate of 10,000 to 15,000 tons a year.¹⁶⁶ U. S. imports began with 55 tons in 1944 but are increasing rapidly; 7225 tons was received in 1947.¹⁷³ Consolidated Minerals, Ltd., Johannesburg, sole producers of the Transvaal andalusite sands, reported sales of 450 tons during the third quarter of 1935.⁸⁵ During the recent war, kyanite, sillimanite, and andalusite were mined from at least two localities in Korea, south of latitude 38°N. About 718 metric tons of kyanite was produced in Korea in 1944.¹⁷³

No substantial imports of kyanite or sillimanite had been received from Australia prior to 1943. In that year, 200 tons of sillimanite was received from New South Wales. In 1944, a total of 346 tons, including 48 tons entering through Canada, was received. The imports in 1945 were 341 tons;⁸⁵ for 1946⁸⁵ and 1947,¹⁷³ respectively, they were 592 and 1163 tons.

There has been a small production of topaz in South Carolina in the past few years. A carload was shipped in 1939, and 583 tons was marketed in 1942. Production and sales increased in each of the following two years but decreased in 1945.⁸⁵

PROSPECTING, EXPLORATION AND MINING

Deposits of the sillimanite minerals are restricted largely to highly metamorphosed areas, although some transportation away from the immediate area may occur. Because of their hardness and chemical stability, they often form low ridges and hills, which aid in their location. Intrusive igneous rocks may cause reconcentration into large pockets or lenses. Such deposits in general are not very productive because sporadic and nonuniform, although some important commercial deposits have been of this type. Nevertheless, residual float boulders attract attention to closely associated and comparatively low-grade disseminations in schists and gneisses. The latter are inclined to be more widespread and uniform, and, with beneficiation, constitute more promising occurrences. Residual soils containing sillimanite minerals may point to underlying deposits, although such float may cause overestimation of the richness of the deposits.

The most promising areas for exploration are those in which deposits, even though uneconomical, have already been reported. The location of the large California andalusite deposit was made in this way, and many other such examples are known. General topography and climate are significant from the standpoint of possible exploitation. The accessibility of the area is an important consideration, although isolated areas should not be ignored. Excavation of pits and trenches,

aided in some cases by core drilling, is advisable in favorable areas, and chip samples should be taken for test. Prospectors are in the habit of sending samples to state and federal survey laboratories, or to interested private firms, for identification and evaluation.

Mining methods are comparatively simple. The mining of residual boulders poses no problem but that of sufficiency of supply. For in situ deposits, opencuts, benches, or short tunnels suffice, only surface and near-surface deposits usually being worked. Jackhammer drills prepare the holes for the dynamite charges used in blasting.

The andalusite ore at White Mountain, California, is mined from large stopes connected by short tunnels. Mining is selective, with hand sorting and frequent checks of specific gravity. The latter have proved of great value in ensuring uniformity of this complex ore. The ore is packed on muleback $4\frac{1}{2}$ miles to the foot of the mountain trail, whence it is trucked 3 miles to the 2000-ton stock piles at the railroad siding.¹¹⁸ At Oreana, Nevada, dumortierite was first obtained by drilling and blasting exposed boulders but later opencuts were made in the hillside and several tunnels were driven. Cobbing, hand-sorting, and specific-gravity checks helped to maintain a high grade of ore.⁶⁰ The vertical andalusite vein at Hawthorne, Nevada, was worked from a 140-ft shaft.⁸⁵ The kyanite at Ogilby, California, was mined from opencuts and tunnels.¹²⁵

Kyanite mining in the southeastern states has been equally simple. Mining at Baker Mountain, Virginia, is from opencuts.¹⁷¹ At Burnsville, North Carolina, the ore was worked from a series of 20-ft benches, which had been blasted parallel to the schistosity.⁷⁶ At Clarkesville, Georgia, surface accumulations were simply shovelled into a flume; placer deposits were stripped of overburden, then worked by pick and shovel; weathered schist was stripped, drilled, and blasted.^{18,40} South Carolina topaz has been mined largely from float material picked up on the surface or dug from the first foot of soil. An opencut has been made to work the vein topaz. Cobbing and hand-sorting are necessary to eliminate quartz.²⁰ Most of the mining of India kyanite to date has been from residual boulder accumulations.⁷⁹

PREPARATION FOR MARKET

The preparatory treatment, if any, depends on the nature, extent, and intimacy of intergrowth of the associated mineral impurities, and on the degree of expansion on calcination. The andalusite ore mined at White Mountain, California, by Champion Sillimanite, Inc., contains no objectionable minerals, since the diaspore, corundum, and pyrophyllite merely add to the aluminosilicate content, and the muscovite and rutile are low enough to be harmless. The dumortierite ore mined by the same company contains about 20 pct of intimately inter-

grown muscovite, which it is neither practical nor necessary to separate. India kyanite contains an average of 10 pct corundum, which actually adds to the refractoriness. Domestic kyanite and topaz usually contain an excess of silica in the form of free quartz, which must be removed or reduced to a minimum. Iron minerals, such as magnetite, limonite, and pyrite, if present in more than traces, must be eliminated. Disseminated kyanite, sillimanite, or andalusite contain at best a subordinate percentage of the aluminum silicate mineral and must undergo beneficiation to effect concentration by elimination of the other schist constituents. Andalusite, sillimanite, and dumortierite are sufficiently volume-constant to require no precalcination. Topaz, although suffering no great expansion on firing, is calcined to remove the objectionably high fluorine content. Kyanite, because of its excessive expansion on firing, is usually calcined before use as near to 1500°C as is practicable. There is a growing tendency to calcine kyanite at still greater temperatures, to produce refractories serviceable at much higher temperatures than heretofore.

At the plant of the Champion Spark Plug Co., Ceramic Division, Detroit, the andalusite ore shipped from California by its subsidiary is crushed and ground, passed over a magnetic separator, and screened into three sizes: 8 to 14-mesh, 14 to 30-mesh, 30-mesh and finer. In making refractories, these three sizes are used in equal proportions, together with additions of electrically fused alumina, both alpha and beta. In making porcelain-type bodies, fine grinding is essential. The andalusite is mixed with fluxes, clays, and water, and reground to pass 325-mesh. After lawning and magnetic separation, excess water is removed by a filter press. Thus the plastic body or slip can be handled and stored in aging cellars for use in forming ceramic products. The slip is spray-dried for processing by special methods. Both refractories and spark-plug insulators are fired in continuous kilns, 300 ft long, at 1480°C, three days being required for passage through the kilns. Dumortierite is treated in the same way as is the finely ground andalusite, and is used with it in spark-plug insulators.

The Kyanite Mining Corporation, Cullen, Virginia, recovers kyanite from complex schists by equally complex but highly efficient modern mineral-dressing methods, giving a concentrate containing a minimum of 90 pct kyanite. High-intensity magnetic separators keep the iron content at a minimum. Current research is designed to increase production at Baker Mountain and to put the Willis Mountain deposit in production. Calcination involves continuous treatment in a rotary kiln at 1480°C till complete mullitization is effected, as indicated by specific gravity and petrographic check. The coarsest product of acceptable purity is 35-mesh. Grinding in a stone-lined pebble mill gives the finer sizes: minus 48-mesh, minus 100-mesh, and minus 325-

mesh, each showing 95 pct passing the designated mesh. Kyanite is sold in both raw and calcined form.¹⁷¹

Typical of the way in which kyanite ores of the southeastern states may be concentrated is the process used by the former Celo Mines, Inc. at its Burnsville, North Carolina, plant. The huge lens of kyanitic gneiss mined there is a uniform but low-grade ore. After crushing, the ore was disintegrated, with almost no grinding, in a special hammer mill. Screening effected considerable concentration of the kyanite, which was held on the coarser screens. An electromagnetic separator removed abraded iron, sulphides, garnet, biotite, and some muscovite. The non-magnetic product was pneumatically tabled to separate the kyanite cleanly from the quartz, feldspar, and muscovite. Finer sizes were produced by grinding in a Silex-lined pebble mill. Calcination was effected in an oil-fired rotary kiln. A sample was taken from each 100-lb bag for specific gravity test.⁷⁶

The Georgia-Carolina Minerals Corporation used very simple methods in treating ore near Clarkesville, Georgia. A surface accumulation of kyanite derived from a kyanite-mica schist was worked until exhausted as follows: The kyanite-bearing top soil was carried by a flume to a mill, where the larger crystals were screened out. Mullers rubbed off adhering mica and quartz grains. Hand picking removed quartz and schist fragments and gave a concentrate running about 3 pct iron oxide and 3 pct quartz. A placer deposit in the valley was worked by first screening out the cobbles, then treating in sluice boxes by scraping the gravel back and forth with hoes to wash out the clay, sand, and fine gravel from the coarser kyanite. Hand-operated jigs recovered finer kyanite escaping with the gravel. Kyanite was also recovered from partly weathered schists by mulling, washing, and screening.¹⁴² The Southern Mining and Milling Co. employed similar methods, involving crushing, mulling, screening, and jigging, to obtain a 95 pct concentrate.¹⁸

The Vitrefrax Corporation developed an ingenious though not too successful method of reducing the quartz in its Ogilby, California, kyanite ore. The ore was heated to about 950°C in a rotary kiln, which reduced the iron oxide for later magnetic separation and converted alpha to beta quartz. Quenching the calcine in water reconverted the quartz to the alpha form. The sudden contraction involved shattered the quartz free from the kyanite. After crushing, the ore was washed over slightly inclined shaking screens, which retained a relatively pure kyanite concentrate.¹¹⁸ This process was later discontinued. A similar process was used in Germany during World War II.²⁷ The Aluminum Silicates Co., present owners of the Ogilby deposits, are doing research to produce an iron-free glass-grade kyanite through flotation and magnetic separation.¹⁷²

The only kyanite deposits generally considered practical to work are the disseminated ores in kyanite schists, which require fine grinding to liberate the kyanite. As consumers come to accept such fine-grained kyanite, commercial exploitation of these schists will become more practical. Froth flotation gives a higher kyanite recovery and concentration from such ores than any other method, and considerable experimental data have been secured.^{92,93,105,148} Similar work on the beneficiation of disseminated sillimanite has been carried out. A schist from Troy, Idaho, containing about 8 pct sillimanite, was crushed to pass 35-mesh and concentrated by tabling and flotation.¹⁴⁰ A South Carolina schist containing 17 pct sillimanite gave 82 pct recovery as a 99 pct concentrate containing 1.04 pct total ferric oxide, by tabling, flotation and magnetic separation.¹⁰⁶ Tests on andalusite ore from Hawthorne, Nevada, required grinding to 48-mesh to obtain liberation, and indicated tabling to be more efficient than flotation.¹⁷⁵ Massive topaz from South Carolina responds well to calcination in a rotary kiln, the optimum temperature being 1480°C. No kiln corrosion or unusual deterioration of equipment was noted, although there is the problem of disposal of the liberated fluorine.¹⁰² Calcination of topaz in commercial kilns has not yet become practicable because of the liberation of fluorine and the accumulation of siliceous deposits on the walls and in the flues of the kiln.

The Corhart Refractories Co. has been producing electrocast mullite-corundum for a number of years. It is obtained by fusing in an electric-arc resistance furnace the proper mixture of such highly aluminous materials as burley fire clays, bauxite, or diaspore clay. The melt is cast into shapes in sand molds and cooled slowly to allow large crystals of mullite and corundum to develop. A small tonnage of waste material from the process is crushed and sized for use in bonded refractories.^{79,118} The Vitrefrax Corporation produced a fused synthetic mullite in somewhat similar manner but with kyanite and pure alumina as the raw materials.⁸⁵

One of the earliest commercial methods for producing "sillimanite" for refractories was the Malinite process. It involved partial reduction of the silica in clays or other aluminous materials by smelting with coke in a cupola furnace.^{74a} Somewhat similar work done at the Bureau of Mines at Seattle, Washington, resulted in volatilization of silica from pure kaolin in an electric furnace, yielding a melt that crystallized largely as mullite with some corundum.¹⁶⁴ An interesting recent development is the production of mullite for refractories and refractory coatings by a variation of the Goldschmidt Thermit reaction, whereby the highly exothermic reaction initiated by heating aluminum metal and clay to about 930°C rapidly raises the temperature to about 1650°C. This process was described in several papers from the New York State

College of Ceramics as early as 1939.^{130,131,132} Claims to discovery of the same process are made in a Russian publication dated 1946.¹⁰¹

During World War II, Germany, cut off from India kyanite, developed a synthetic "sillimanite," which gave good service. A mixture of clay, aluminum trihydrate, fused alumina, feldspar, and water was mixed, extruded, cast into small blocks, dried, and fired $4\frac{1}{2}$ to 5 days at 1600°C. The calcine was crushed for use in refractories. Its cost was almost three times that of India kyanite.⁶¹ This development did not mark an innovation, for the first ceramic application, which originated at the Bureau of Standards even prior to publication date of 1918, involved the use of synthetic sillimanite prepared by blending 258 parts of kaolin and 102 parts of anhydrous alumina, which, after suitable processing, was calcined at cone 20.^{8,111} From 1919 until andalusite was available in 1922, the Champion Porcelain Co. prepared and used many tons of synthetic sillimanite produced in similar manner.

TESTS AND SPECIFICATIONS

Various tests may be found useful in evaluating samples of these minerals. Checking specific gravity of the ore as mined did much to assure uniformity of grade of California andalusite.¹¹⁸ Gravity separation on a macroscopic^{76,140} or microscopic³³ scale has been helpful in determining grade of ores and concentrates. Flotation tests have been used to determine roughly the tenor of disseminated sillimanite.³² Petrographic analysis gives a rapid check of the approximate mineral composition of powdered ores. Freedom from associated minerals is not always essential. Such minerals as corundum, diaspore, and pyrophyllite may even be beneficial.^{56,79} Although alkali-bearing minerals adversely affect electrical and load-bearing properties, moderate amounts of muscovite may be tolerated. Quartz, because of its inversions, should be kept as low as possible. Rutile, a common accessory, is not a flux, but its iron causes discoloration at high temperatures. However, a very small amount is permissible.

Iron compounds are objectionable because of fluxing and discoloring action. For use in the glass and electrical porcelain industries, the iron content should not exceed 0.2 pct. Chemical analysis gives a check on iron, alkali, and titania contents, besides yielding the alumina-silica ratio.

Inspection of lumps in ultraviolet light aids in distinguishing various minerals present.³⁴ Calcination also emphasizes distinctions between minerals and allows observations on fluxing, discoloration, and expansion tendencies.³⁵ Test bars made with suitable binders, fluxes, and mineralizers are useful in studying load-bearing properties at high temperatures. Cones formed from the powdered ores may be used to determine refractoriness. Sample standard bricks or test pieces serve for

measurement of shrinkage, porosity, absorption, and spalling. Considerable information on such tests is given in the literature.^{37, 70, 79, 112, 120, 150} For use in refractories a hard, tough grog of low porosity, from $\frac{1}{4}$ -in. down in size, is desired. For this reason refractory makers specify massive India kyanite in preference to the coarse, bladed domestic types, which yield a fragile, high-porosity grog. When sillimanite enters the industrial picture, the massive or coarse prismatic types will probably be specified over the finely fibrous variety because of the advantage of coarser grog size.

USES

Kyanite, because of its wider occurrence in commercial quantities, has been the most widely used of the sillimanite group. It has been employed, principally in refractories, in the metallurgical, enameling, glass, ceramic, chemical, electrical, and cement industries. The metallurgical industry consumes about 50 pct of such kyanite products in the United States while the glass industry uses about 40 pct, the remaining 10 pct going into miscellaneous products.^{20, 51} Among metallurgical uses are furnaces for melting high-copper brasses and bronzes, copper-nickel alloys, some steels and ferrous alloys, and zinc-smelting and gold-refining furnaces. Appreciable amounts are used in parts of heat-treating furnaces and in the roofs of many small direct-arc electric furnaces. It is also used in the superstructure of glass tanks as well as below the slag line, and in plungers, feeders and other glass-house refractories. In addition, appreciable quantities of kyanite are used as a glass-batch constituent, to increase the alumina content. It is excellent for the construction of laboratory kilns operating at unusually high temperatures, as well as general commercial kilns. It is used in linings of enamel melters and cement-clinkering kilns; in plastic ramming mixes, saggars, and other kiln furniture, special refractory shapes, and electrical porcelain.

Andalusite and dumortierite have been practically limited in use to the firm controlling the only major domestic sources, the Champion Spark Plug Co. The chief use of andalusite has been in spark-plug insulators, many millions of which have been made with andalusite in the past 25 years. Other applications have been Dressler-kiln muffle chambers, expansion sleeves, pyrometer protection tubes and burner parts, which have withstood temperatures of 1650°C or higher continuously for 13 years. Kiln car tops, removable kiln crowns, saggars, ramming mixes, glass-house refractories, electric-furnace refractories, extrusion dies, mill balls, mill linings, pyrometer tubes, and laboratory ware have also been made. Dumortierite has been used mainly in spark-plug insulators, and laboratory porcelain, although tests have indicated its merits in refractories and other ceramic bodies.^{26, 116, 117, 123, 162}

Topaz has been used in the steel industry as a substitute for fluorite

as a slag thinner, and is very useful in leadless glazes⁸⁵ and as a glass opacifier.⁸² It has given good results as a substitute for India kyanite in superduty refractories.⁷⁹ It is also promising in the raw state as a bond for domestic kyanite.⁷⁸ Topaz refractories in use in the glass industry are showing promise. Topaz brick are being tested in malleable, heat-treating, and high-temperature furnaces, open-hearth checkers, electric-steel melting furnaces, vertical lime kilns, coking furnaces, gray-iron cupolas, frit furnaces, boiler side walls, and welding and forging furnaces.²⁰

In this country, little use has been made of sillimanite, although sample bricks meeting the most rigid requirements of heavy-duty refractories have been fabricated.³⁷ Synthetic sillimanite has been used in spark-plug insulators, pyrometer tubes, and laboratory porcelains and as a substitute for India kyanite in refractories.⁶¹

Fused-kyanite mullite has been used in spark-plug insulators and as a grog in refractories. Electrocast mullite has found its main use in monolithic glass-tank block and other glass-house refractories where erosion is particularly severe. High cost and spalling tendency react against its use in small cast shapes, although some has been used as grog in bonded refractories.

MARKETING AND PRICES

The Kyanite Mining Corporation markets raw and calcined Virginia kyanite in grog sizes of 35-mesh and less. The Chas. Taylor Sons Co. distributes raw lump and ground calcined India kyanite. The Golwynne Chemical Co. and Mullite Refractories Co. market both India and Africa kyanite ores.¹⁶⁷ Some India kyanite is also imported and marketed by H. H. Davidson, New York City.¹⁷⁴ The P. B. Sillimanite Co., Ltd., distributes both India and Africa kyanite ores and products in Great Britain.

The Champion Spark Plug Co. has marketed andalusite refractories as Champion Sillimanite, and its spark-plug insulators bear the name "Champion." The New Castle Refractories Co. markets kiln furniture containing andalusite. Refractory products of the Vitrefrax Corporation were sold under the names Vitrox, Argon, and Durox.⁸⁵ The Chas. Taylor Sons Co. distributes India kyanite and its products as "P. B. Sillimanite." Mullite Refractories Co. sells such products under the name Shamva. The latter two companies also market products using Africa and domestic kyanite, as do also Richard C. Remmey Son Co., Laclede-Christy Clay Products Co., General Refractories Co., and Denver Fire Clay Co. The Coors Porcelain Co. uses India kyanite, while the A. P. Green Fire Brick Co. and Ironton Fire Brick Co. employ domestic kyanite in their products.¹⁶⁷ Doubtless other companies than those listed market kyanite-bearing refractories.

When first introduced about 1923, kyanite sold for \$100 a ton (short ton, unless otherwise specified) but soon reduced to \$40 a ton. In 1935, impure domestic dornick ore sold for \$10 per ton, and \$25 to \$36 was asked for high-grade concentrates. Imported kyanite f.o.b. Atlantic seaports sold for less than \$20 per ton. Just before the war, in 1939, domestic kyanite sold for \$15 to \$78 per ton, depending on purity, grain size, and whether calcined or raw. In early 1943, prices of domestic kyanite were placed under control of the Office of Price Administration (OPA) and ranged from \$19 for 35-mesh raw kyanite to \$42.50 for 325-mesh calcined material. The price per ton for each grade was increased \$5 late the same year and remained at the higher levels till the end of 1945.⁸⁵ Prices quoted by Kyanite Mining Corporation in its price list of Aug. 15, 1946, indicate a further increase of about \$5 per ton. Cost of calcining decreased from \$15 per ton in 1934 to \$7 per ton in 1946. As of Aug. 31, 1948, the quotations on domestic kyanite at point of shipment per ton were: crude, \$20; 35-mesh, \$37.50; glass grade, \$40 nominal. The cost of crude India kyanite increased from about \$25 per ton f.o.b. Atlantic ports in 1940 to \$54 per ton in 1942.⁸⁵ The present price varies between \$50 and \$55 per long ton of crude ore, with African kyanite bringing \$33.50 per ton, and calcined, ground, and packed India kyanite selling for \$104.50 per ton.¹⁶⁷ A nominal price of \$50 per ton has been placed on andalusite and dumortierite at the mines of Champion Sillimanite, Inc.

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PERSONAL COMMUNICATIONS

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169. Letter from Dr. E. Wm. Heinrich, University of Michigan, Ann Arbor, Michigan, dated Oct. 21, 1947.
170. Letter from Herbert Hornkohl, Caja de Credito Minero, Santiago, Chile, dated March 30, 1947.
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174. Personal communication from H. W. Ryland, Coors Porcelain Co., dated Nov. 5, 1947.
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CHAPTER 43

SLATE

BY CHARLES H. BEHRE, JR.*

SLATE (*Thonschiefer*, German; *ardoise*, French) is a rock, an aggregation of mineral grains, occurring in nature, which is used for roofing and other special purposes. It is finely granular and crystalline and generally derived from an originally clayey bed or series of beds. As a result of its having been put under essentially horizontal compression by geologic forces, this material now has its particles elongated and flattened so as to yield a very good rock cleavage along the flat surfaces of the minerals, a feature entirely independent of the original bedding in the rock. This is the gist of the definition adopted by the Committee on Slate of the American Society for Testing Materials.

Slate differs in varying degrees from most other common rocks (such as limestone, sandstone, granite, and "trap") in chemical and mineral composition. Its most characteristic feature, however, is its tendency to fracture along a series of very nearly parallel and very closely spaced smooth planes, called cleavage planes. This property of cleaving, above all else, gives slate its industrial value.

ORIGIN AND MODE OF OCCURRENCE

Most of the features of slate might be anticipated from its origin. Being a rock rather than a mineral, its composition may vary considerably without impairment of value. In most slates, the material of which the rock is now composed was once deposited as clay on the bottom of a lake or sea. Subsequently these clayey strata were compressed by the kind of lateral pressure that folds rock strata, the minerals of the clay being changed or metamorphosed. In the chemical reaction involved, new and essentially plane-shaped minerals belonging to the mica groups were developed. Other minerals were formed but micas generally predominated. These were oriented so that their two longer dimensions are approximately at right angles to the last effective direction of pressure. Since the crystals are thus subparallel, fractures can be developed easily along their surfaces, much as cards can be separated by inserting a knife blade between them.

For the foregoing reasons, slate is found in noteworthy amounts

* Professor of Geology, Columbia University, New York, N. Y.

only where: (1) the original strata were largely clayey, and (2) where there has been sufficient rock folding to induce recrystallization. Hence, for example, no commercial slate is found in the central Mississippi Valley; shales in that region have nowhere been sufficiently intensely folded to yield slate.

COMPOSITION

Chemical Composition—Chemically, slates are generally fairly uniform. Analyses given by Hirschwald¹⁶ show the extremes of possible composition as follows. Al_2O_3 , 12 to 26 pct; MgO , 1.07 to 5.47; SiO_2 , 35 to 59; Na_2O , 0.53 to 5.98; CaO , 0.14 to 17.75; CO_2 , 0.11 to 11.81. In addition, FeO , Fe_2O_3 , TiO_2 , MnO , BaO , Li_2O , P_2O_5 , SO_3 , ZrO_2 and H_2O may be present,^{11,16,32} generally in minor amounts. Of the constituents mentioned, much of the silica is combined with alumina and with basic oxides to form complex silicates (represented by minerals of the mica and chlorite groups). The carbon dioxide is a constituent of carbonates. Some carbon may be present in organic compounds or as elemental carbon derived from organic matter. Other representative analyses are given by Dale,¹⁰ Hirschwald,¹⁶ and Behre.³ The general preponderance of potassa over soda in the analyses is probably the result of base exchange and selective adsorption.²⁷

Mineralogic Composition—From the utilitarian viewpoint, the mineralogy is of more interest than the chemical composition, for mineralogy rather than chemistry determines perfection of cleavage, insulating qualities and strength. The chief minerals in slate are present in approximately the following quantities:³² muscovite, 38 to 40 pct; chlorite, 6 to 18; quartz, 31 to 45; hematite, 3 to 6; rutile, 1 to 1.5. Other common minerals are the carbonates (calcite, dolomite, siderite and mixtures), kaolinite or related minerals (especially if the slate is not highly metamorphosed), graphitic carbon, biotite, various feldspars, andalusite, pyrite, and magnetite. Dale¹¹ gives a much longer list but many of the minerals mentioned by him are very rare or are primary and adventitious to any rock derived from a sediment.

PROPERTIES

As a structural material, slate has properties, such as hardness, crushing strength, and density, in common with other building stones. Certain properties of particular significance in slate are discussed in the following paragraphs.

Color

The consumer's taste in color of roofing slate varies greatly with time and locality, therefore color is very important commercially. Slates may be deep brick red, grayish purple, olive green, gray-green, dull bluish green, brownish (owing to strains of hydrous ferric oxide), or

mottled in various combinations of these colors. The commonest color is a bluish gray—"slate gray." Not all bluish-gray slates, however, show the same tint; some have a silvery, light gray tone; others are almost black.

Color differences are due to presence of certain mineral constituents, such as hematite (ferric oxide) in red slates, ferrous compounds and chlorite in deep green slates, sericite in light green and gray slates, and graphitic carbon in black slates. As the original mud from which the slate was made was deposited in layers of varying composition, and as the cleavage pieces or blocks of the slate break *across* the bedding (as explained below), individual blocks may show bands differing in composition and hence in color. The most characteristic contrast in such cases is between the lighter and the darker, carbon-rich bands or "ribbons." Other contrasts are in the "mottled" slates, in which blotches of red or purplish colors appear on a generally green surface, or vice versa; these are largely caused by mineralogical differences produced by metamorphism but they may result also from weathering, in which case they disappear in depth.

The color of slates is not always "permanent" but even exposure to the weather for as much as 20 years, as on a roof, may result only in a change in shade of the original color, designated as "color-aging"³ to distinguish it from the steady disintegration of several centuries, which affects slate as it does any other stone. Most color-aging is probably due to alteration of iron sulphides, of iron oxides,¹¹ of carbon and carbon compounds, and especially of the most soluble and least resistant minerals, the carbonates, notably when these contain iron.^{3,11} Thus it may safely be said that most color-aging effects result from changes in ferruginous minerals and are not generally deleterious to structural use.

Cleavage and Grain

There is still uncertainty as to the acceptability of the various theories for the origin of cleavage. In recrystallization of shale to slate, the newly formed platy minerals, especially mica, tend to be arranged approximately at right angles to the deforming pressure.⁴ Some minerals such as quartz, not capable of this sheetlike elongation, yield to a linear or pencil-like but parallel elongation in planes parallel to the mica "sheets." In consequence, thin sections of slate show varying characteristics, depending upon their orientation. Microscopic views of thin sections in the plane of the cleavage show lathlike patterns; those at right angles to cleavage but in the plane, thin bands representing sections cut parallel to the long dimension but across the flat sides of the laths; and those at right angles to both cleavage and grain, end views of the laths. Parting parallel to the mica sheets (or laths) and

along one long dimension of the pencil-shaped minerals yields the cleavage. The parallelism of the pencil-shaped crystals, like quartz, also makes it possible to break slate at right angles to cleavage; such far less regular planes of fracture are the grain planes. Grain planes, therefore, are generally normal to the cleavage planes. As a rule, the cleavage planes are parallel to axes of the folded beds (Fig 1). For a given region the trend or strike of cleavage and of grain is fairly constant, varying as a rule not over 10° .

False Cleavage, Shear Zones and Related Features—If the cleavage itself is later deformed, it may show wrinkling or fracturing—minute, closely parallel wrinkles or cracks on the cleavage surface of the slate.

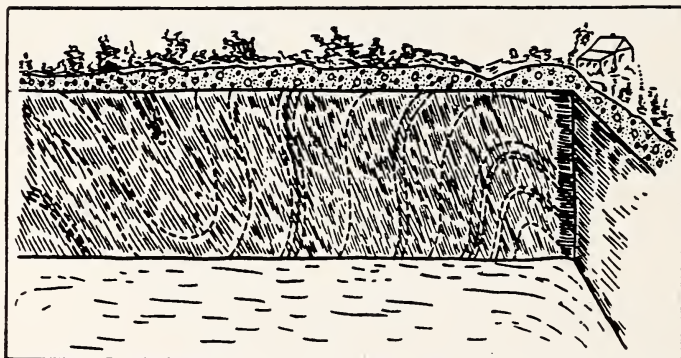


FIG 1—STRUCTURAL FEATURES OF SLATE AS SEEN IN QUARRY WALL, EUREKA QUARRY, SLATINGTON, PENNSYLVANIA.

Two adjacent folds are outlined by the bedding. The cleavage inclines steeply to right, generally parallel to axes of folds.

When an attempt is made to split such slate into thinner slabs, it breaks across the cleavage into irregular, worthless slivers. The resulting fractures are called false cleavage, or, if massed, cleavage shear zones.

Jointing—Joints are rock fractures having various causes. They are smooth-walled, regular, open crevices; or curved openings, especially where crossing from one layer to another; or crevices that have since been filled with mineral matter. In many slate regions they are highly regular in pattern. A group of joints may be approximately parallel, all inclining or dipping in a single direction. Such parallelism may help in quarrying; on the other hand, numerous joints cutting the cleavage make difficult the winning of large, unfractured blocks from the quarry.

Bedding

Like all rocks originally deposited in layers or strata, slate generally shows traces of stratification or bedding, however much deformed or concealed by subsequent recrystallization. This is important from a practical viewpoint because: (1) as explained, in some slates the suc-

cessive layers differ in composition; therefore the slate tends to break parallel to the bedding, which may be transverse to the cleavage (Figs 1 and 2); (2) the color and other properties in many slates change from bed to bed; thus blocks quarried from differing beds, even in the same quarry, may show desirable or undesirable qualities.

Conductivity and Resistivity

Slate is generally a good heat and electrical insulator. The property of electrical insulation makes slate highly valuable in switchboards and similar places. The chief characteristics of beds serving as

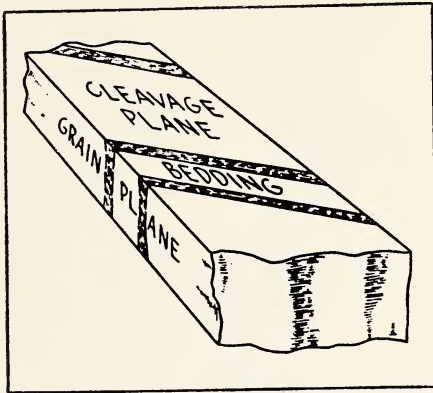


FIG 2—STRUCTURAL FEATURES OF BLOCK OF SLATE AS QUARRIED.

electrical insulators are: (1) uniformity in the size of the mineral grains and in the mineralogical composition of the slate as a whole, and (2) the absence or relative paucity of certain highly conducting or highly nonconducting minerals, especially magnetite, pyrite, graphite (especially if in locally dense areas), and quartz (especially when highly localized).³

DISTRIBUTION OF DEPOSITS

The valuable slate deposits of the world are by no means the only slate deposits known; they are simply those that occur near enough to a considerable market³⁵ to merit working on a large scale. Therefore, virtually all slate deposits that are commercially important are within easy reach of populated regions.

Table 1 shows production of slate by countries for certain years. These data, though not recent, typify peacetime production.

United States

Slate is quarried in small amounts in several localities in the western United States,¹¹ notably central Colorado; western Nevada; near Phoenix, Arizona; near Placerville, California, and at Provo, Utah.

TABLE 1—*World Production of Slate*^a
METRIC TONS UNLESS OTHERWISE INDICATED

	1928	1930	1932	1934	1935	1936	1937	1938
Australia.....	2,053 c	943	229	7,201	31,434 c	1,268 c	2,602 c	2,729 c
Belgium (pieces).....	nil	136	227	16,520,000	1,147	1,131	816	994
Canada.....	276,490	260,800	195,900	154,900	156,900	152,420	136,780	131,000
France.....	123,082	42,151	51,622	100,934	90,996	118,516	117,656 ^c	67,208 ^a
Germany.....	305,055	264,705	256,899	295,103	307,752	301,852	290,018	289,875
Great Britain.....	9,297	8,641	8,483	10,341	11,328	10,090	9,370	13,741
India, British.....	18,650	c	c	c	c	c	c	c
Italy.....	\$224,985	c	c	c	c	c	c	c
Japan.....	c	12,232	64,132	c	c	c	c	c
Spain.....	1,185	2,723	2,699	2,577	2,839	2,765	2,517	2,390
Sweden.....	\$ 38,640	\$85,050	£16,775	305	439	£17,357	£31,030	£35,568
South Africa.....	586,377	420,580	257,862	211,087	292,508	412,558	403,205	446,978
United States ^b	c	c	c	102,000,000	164,000,000	c	c	c
USSR (slabs).....								

^a Slightly amended from Mineral Industry during 1934 and Mineral Industry during 1941 (G. A. Roush, editor). New York, McGraw-Hill Book Co.

Data for but few countries available since 1938. Foreign production since 1941 not available.

^b Amount sold.

^c Figures not available.

^d Norway and Portugal are important producing countries not here listed because production data are not available.

^e Data incomplete.

The eastern states, however, contain the best developed slate deposits. Minor deposits are in the Ouachita Mountains of Arkansas,³¹ in northwestern Georgia,³⁵ and in southeastern Tennessee,¹¹ northern Minnesota, and New Jersey. None of these areas has noteworthy production at present, however. The five outstanding slate regions in the United States (Fig 3) are described in the following paragraphs.



FIG 3—GENERALIZED MAP OF CHIEF PRODUCTIVE SLATE BELTS OF THE EASTERN UNITED STATES.

The Maine deposits are near the middle of the state, chiefly around Monson. The slate is of early Paleozoic age and is dark bluish gray with a purplish cast. The nearly parallel position of bedding and cleavage for great distances is surprising.¹¹ Though not a major source of slate, Maine has for long been an important producer of electrical slate and of minor amounts of roofing and structural slate.

The Vermont-New York slate region¹⁰ is the second most important in the United States. The slates are Ordovician and Cambrian in age. They are greenish gray, purplish, variegated (i.e., greenish gray and purplish, mixed), and deep brick red. Some of the green slates are “unfading,” while others (“sea green”) become less green and more gray upon prolonged exposure. This region usually stands second in the production of roofing and structural slate and is an important producer of electrical slate. Its colored slates, the only colored slates available in the United States, are especially desired for roofing and for floor tile and flagging.

The slate region of eastern Pennsylvania, centering around Bangor, Pen Argyl, and Slatington, is the most important in this country.^{2,3} Much of this slate is banded in various shades of gray, the dark gray bands being narrower and richer in carbon. Banding is widely spaced in the "soft vein" part, but narrow in the "hard vein" part of this region. The gray color makes this slate excellent for blackboards, bulletin boards, and school slates. The region furnishes the greater part of the nation's roofing slate and about 90 pct of its structural slate.

The Peach Bottom region^{3,25} produces minor amounts of roofing slate and some structural slate. It extends northeastward across the line separating Pennsylvania and Maryland, centering around Cardiff and Delta. The slate is assigned to the pre-Cambrian,²⁰ and is closely folded; structural details are not clear. It is an excellent roofing slate, lustrous and of dark blue-gray color. An important product in recent years has been slate granules.

As described by Watson⁴¹ and Dale,¹¹ the Virginia slate region may be grouped into three belts, the eastern being of Ordovician, the central and western belts of Cambrian age. The slates are mostly dark gray with faintly greenish or brownish tints and are highly lustrous, but some dark greenish gray and variegated slate has also been quarried. Virginia slate is used chiefly for roofing and granules. The main center of production is in Buckingham County.

Canada

Production of slate in Canada³⁰ is not of large volume. In Madoc Township, southern Ontario, a good blue-gray slate is known. In New Brunswick and Nova Scotia, slate deposits of commercial grade occur, but only those in Halifax and Hants Counties, Nova Scotia, are worked. The leading slate districts in Canada are in eastern Quebec, extending from Megantic County southwest to Brome County; these slates are of Cambrian age and are chiefly blue-gray, but some are a deep maroon or a light green color. Operations began as early as 1854 but production is now virtually at a standstill. Slate reported from the western provinces is not of economic importance at present.

Europe

The leading slate-producing countries of Europe,¹⁷ as judged by recent production figures, are Great Britain, France, Belgium, and Germany. Slate is produced also in noteworthy amounts in Czechoslovakia, Italy, Norway, Portugal, Spain, and Switzerland.

The two outstanding slate districts in the British Isles are Wales and Cornwall. The Welsh quarries and mines are chiefly in Carnarvonshire and Merionethshire; they are opened in Cambrian and Ordovician rocks. Slates of the former age are green, purple, and red in color;

of the latter age, generally gray or black. Near Delabole, in Cornwall, high-grade slates of Devonian age and bluish gray color are produced. This slate is excellent, but the industry is smaller than in Wales. Slate is also quarried in Scotland, in the Lake district of northern England, and in Ireland.

In France, the chief producing centers are along the Meuse River (Department of the Ardennes) on the north central boundary near Belgium, and in west central France near the Loire River, in the Department of Maine-et-Loire. Typically the Maine-et-Loire slates are tough, blue-gray in color, and of Ordovician age. In the Ardennes district, they are of Cambrian age, and are purplish, red, green, grayish green, and black. Some are especially rich in magnetite.

In Germany, the principal slate production in recent years has been in Thuringia and Prussia, with small amounts from Bavaria. Chief producing centers are Bundenbach, Kirn, and Caub, all in what was extreme eastern Germany before World War II; Lossnitz, in Saxony; Nuttlar, in Westphalia; and lesser centers in Thuringia. Most of the slate is blue-gray and of Devonian age. Some is a clay-slate, not wholly metamorphosed into true slate.

The Czechoslovakian slates are greenish and bluish gray; they are largely Devonian in age though in part Mississippian. The Norwegian slates are partly green, partly gray. The slates of Portugal are largely dark gray. Coreglia and Rapallo are important slate-producing centers in Italy.

Other Regions—Slate deposits of more than local importance occur in Japan, India, the Union of South Africa, and South Australia.

POLITICAL AND COMMERCIAL CONTROL, PRODUCTION AND CONSUMPTION

Slate is widespread, almost all larger countries containing at least some deposits, usually in quantities far exceeding domestic needs; therefore political and commercial control of a given slate deposit rests with the country in which it is found. The only exception known to the writer is a large deposit in Portugal, said to be commercially controlled by British capital.

There are virtually no estimates of reserves available even for the most closely studied districts.^{3,6} Because slate deposits are so widespread and large, the quarrying or mining of slate in any given district generally ceases not because the reserves are used up but because of a shift in demand.

Production usually centers in localities favored by factors other than the mere occurrence of workable slate; therefore the discussion of all slate deposits is largely a description of the centers of production.

Like other structural materials, slate finds its greatest demand in

regions of dense population and high industrial development. Hence the United States, Great Britain, Germany, and France are conspicuous consuming as well as producing countries. Great Britain and the United States are the leading consumers; making reasonable assumptions, the approximate value of the slate used in 1938 (the last "normal" year) were £1,919,000 for Great Britain and \$5,505,000 for the United States, according to the U. S. Bureau of Mines and The Mineral Industry. Domestic production, not including granules and flour, during recent years is given by the U. S. Bureau of Mines as shown in Table 2.

TABLE 2—*Dimension Slate Sold by Producers in the United States, 1942-1947*

Year	Roofing			Mill stock		Other ^a		Total	
	Squares	Approximate Equivalent, Short Tons	Value	Approximate Short Tons	Value	Approximate Short Tons	Value	Approximate Short Tons	Value
1942	192,070	71,400	\$1,704,053	18,720	\$1,112,426	16,910	\$139,328	107,030	\$2,955,807
1943	96,220	35,370	841,750	15,950	938,368	21,990	166,231	73,310	1,946,349
1944	89,090	32,750	802,179	12,440	715,689	15,760	203,090	60,950	1,720,958
1945	101,300	38,240	976,122	11,520	742,345	19,900	253,273	69,660	1,971,740
1946	146,790	56,240	1,982,928	12,150	1,032,584	27,860	403,990	96,250	3,419,502
1947	170,590	64,350	3,094,780	13,550	1,444,835	34,610	537,705	112,510	5,077,320

^a Includes flagstones, walkways, stepping stones, and miscellaneous slate.

PROSPECTING AND EXPLORATION

The fundamental facts underlying intelligent prospecting have been summarized by several authors both for building stones in general^{24,34,38} and for slate in particular.^{1,3,6,11,13}

Geologic Factors and Their Applications

An ideal slate quarry should have but little overburden. It should yield only a moderate amount of water. The slate itself should include no conspicuously siliceous or carbonaceous beds and no small masses especially rich in carbon or quartz or other specific minerals (such as magnetite) irregularly distributed; in short, the beds should be uniform throughout their sequence. The strata should stand nearly vertical and have a constant dip or inclination. The slaty cleavage should dip at a low angle to the bedding; and ideally the cleavage should dip at a low angle to the horizontal as well, so as to facilitate quarrying; these two conditions may be mutually exclusive, in which case steep bedding is the less objectionable. Ideally, the beds should trend or

strike at right angles to the grain and parallel with the cleavage. The joints should be regular and preferably parallel in strike with the strike of the beds; ideally also the joints should dip so as to form an angle of 90° with the dip of the cleavage. Prospecting aims at finding a site where the relations mentioned occur to as great a degree as possible. A full discussion of these matters has been presented elsewhere.¹

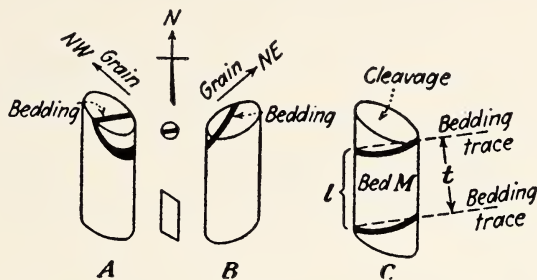


FIG 4—ILLUSTRATION OF USE OF DRILL CORES.

A and *B*, orientation of cores. When regional grain and cleavage trends are known, core is turned so that grain in core is parallel to that in region; thus, if regional grain trends to northwest and regional cleavage (represented by top of core) is to southeast, *A* is the correct, *B* the incorrect orientation of core. Notice effect of orientation on dip of beds. Small figures are profile and top views of core. *C*, determination of correct thickness (t) of bed *M*, as contrasted with distance from top to bottom (l) when measured parallel to length of core. Notice that t is never greater than and usually is less than l .

Exploration by Means of Surface or Near-surface Data

If the slate strata crop out, the foregoing considerations, coupled with the necessary testing of the slate and weighing of the commercial factors, will tell whether quarrying is justified. If there is an overburden of soil, gravel or weathered slate, trenches may be dug, directed at right angles to the layers, to expose as many strata as possible.

Core Drilling—In the United States, core drilling has been used with some success. Shot and diamond drilling are both employed. The former is less costly per foot drilled but the latter can more easily be directed at an angle to the vertical, an important factor. Attention to grain, cleavage, and bedding may combine to make possible a proper interpretation of the core, even if it happens to be turned in removal from the hole (Fig 4).

PRODUCTION METHODS

Production methods have been well discussed in several publications.^{7,36} Though the dates on such references go back two decades, there has been little change since then. What follows is a brief treatment only.

Methods for Breaking Rock—For various reasons slate must be quarried more carefully than much other rock. Blasting, because it shatters the rock, has therefore been progressively supplanted by the other methods. For blasting, black powder is preferred.

Drilling is a necessary preliminary step in most quarrying. Drilling is by power drill, the holes being placed, if possible, in the less valuable beds, to reduce waste. Rates of drilling vary; about 15 fph is an average

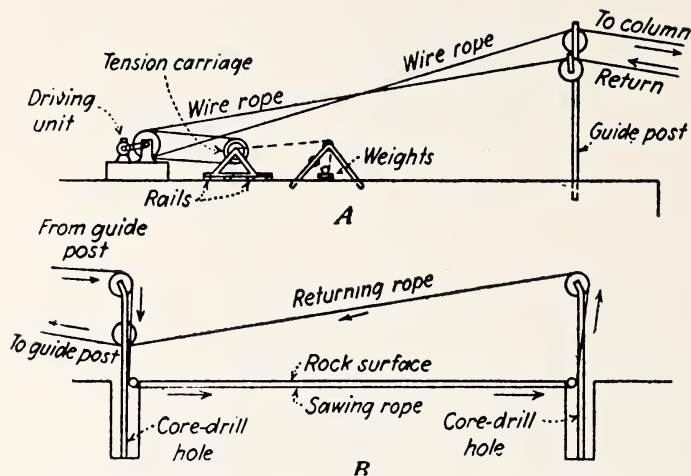


FIG 5—DIAGRAM OF WIRE SAW, MODIFIED AFTER BOWLES.
A, driving end; B, cutting end.

figure. In wedging parallel with the cleavage, metal wedges are forced into the slate by blows with a sledge hammer. Preliminary drilling may be necessary. In quarries in the United States, track channelers were formerly favored, especially in resilient, tough slate. Obviously they could best be used where the cleavage dip of the slate is nearly horizontal.

In Europe, the wire saw has been used for some time, and since 1928 it has increasingly found favor in America, where it is now preferred over all other methods. The "saw" is a twisted steel cable running as an endless belt. Recently the use of a single-strand wire has been especially advocated.⁹ Sand and water fed upon the wire serve as the abrasive. The wire is driven by passing over one or two sheave wheels and over a tension device, which keeps it taut. Depth is acquired by two holes drilled into the rock by a 36-in. core drill (Fig 5). Into these holes, standards are placed, along which the sheaves carrying the wire are progressively lowered. The method eliminates shattering and reduces waste.⁶

Removal of Blocks—Typically the blocks are set free at the quarry walls by channeling, drilling and blasting, drilling and wedging, or

sawing with the wire saw. The overburden having been removed, there remains only a single surface, that below, which is yet to be broken free before the block can be hoisted. This freeing is generally done by wedging along the cleavage surface. Chains are attached to the block and it is hoisted out of the quarry. Maximum weights of blocks handled usually do not exceed 2 tons in American quarries. Hoisting machinery resembles that used in quarrying other kinds of stone. From the landing the slate is transported to the "factory" where it is to be fabricated.

Slate Mining—Where the desired slate beds are thin or the overburden great, handling of much waste is obviated by underground mining. This is done in Wales,⁶ Germany,³⁷ Pennsylvania, and Maine. The methods used do not differ greatly from other mining. Where beds are thin and horizontal, pillars are left to support the roof. Where beds are thin but nearly vertical (as locally in Germany), the openings are filled with waste rock for support.

Effect of Geologic Features on Quarry Methods—Quarry methods vary with differing geologic features. Thus, where the cleavage dips steeply, wedging cannot readily be used for lifting blocks from the quarry floor. Where the beds stand vertical, certain beds are selectively quarried; if they are nearly horizontal, the proportion of waste in quarrying is likely to be great in gaining access to deeper, more valuable beds.

Waste Disposal—The proportion of waste has been variously estimated at 60 to 85 pct of the slate quarried. Hence much research has been aimed at both avoidance and utilization of waste. "Marbleizing" (see end of next section), crushing, and pulverizing represent three approaches to waste utilization. Recent experimentation in the use of powdered or crushed waste as aggregate have also attracted much attention.¹⁰

PREPARATION FOR MARKET

For most uses, slate requires a high finish. The relatively great cost of slate per unit is due largely to this need for finishing before marketing. Blocks of slate are reduced to workable sizes with iron circular saws 2 to 4 ft in diameter and $\frac{3}{8}$ in. thick, turning about 5 rpm. No abrasive is used. Lately there has been much success in retipping sawteeth with special hard alloys. Still more commonly, saws with removable teeth, locked in place by means of a "key," have supplanted other kinds; such equipment, though more costly, has a far longer life than the fixed-tooth saw. The large slabs produced by the circular saws are next accurately cut to specified dimensions by rapidly rotating thin carborundum wheels, or, in the past 5 years or so, by diamond-dressed thin-bladed sawing wheels. Many actual tests have shown that diamond saws have a far longer life, though their initial cost is greater.

Slate blocks are split by hand parallel to the cleavage. Mechanical splitting devices have not proved satisfactory. Desirable large blocks are carefully split for blackboards and small blocks for roofing or school slates. The tools used are thin-bladed chisels or wedges, hand-driven. For roofing slate, the thinly split slab is cut to dimension by shear-like blades propelled by a treadle, by a central shaft and cam, or by individual electric motors. In American practice, a block to be finished for structural uses is planed by means of a straight-bladed knife, mechanically scraped over the cleavage surface of the slate. For finishing slabs for blackboards or for certain structural purposes, the cleavage surface is smoothed with sand on a rotating iron rubbing disk; or by a mechanically moving abrading head; or by hand honing. Slate may be drilled for screw holes and the pieces fitted together into such equipment as tubs, basins, and switchboards. Roofing slates are punched for nail holes.

Much slab slate is surfaced either with oil, varnish, or black enamel. In England, roofing-slate surfaces are being stained with colloidal oxides of iron and manganese. In the United States, the surface of a structural slate may be "marbleized," that is, covered with enamel, patterned, for example, in imitation of marble.

TESTS

Numerous publications deal with the testing of building stones in general,^{1,17,18,26,39} and of slate in particular.^{3,6,12} Hirschwald's discussion,¹⁷ though somewhat outdated, is especially recommended as a source for comparisons between slates. Systematic testing methods have also been developed lately under the auspices of the American Society for Testing Materials.³⁴ What follows presents the subject of slate testing in the briefest possible form; details are given in bibliographic references.

Properties of slate of conspicuous commercial importance are: (1) cleavability, (2) color and its constancy, (3) density, (4) porosity and absorption, (5) hardness, (6) toughness, (7) transverse and crushing strength, (8) elasticity, (9) electrical resistance, and (10) corrodibility. The quarryman is primarily interested in Nos. 1, 2, 5, 6, and 8. The consumer of roofing slate is chiefly concerned with Nos. 2 and 6. For structural uses, Nos. 2, 4, 5, 6, 7, 8, and 10 are of greatest interest, and for electrical purposes No. 9 is paramount. Tests developed for properties 1 and 2 are largely empirical, though tests for color and color constancy have been devised by the National Bureau of Standards.

Specific gravity (or density) is most accurately measured by weighing and obtaining the volume with a volumeter¹⁷ or by means of a Le Chatelier flask.¹⁹ Hardness of slate, whether the stone is to be used

in pieces or slabs or in crushed particles, is best tested by means of a sclerometer^{15,17} or Deval abrasion machine.^{30,32} Toughness is tested with a plunger that drops from a given height.⁴⁰ Tests for crushing strength, transverse strength, and elasticity, and for porosity and absorption^{17,19,41} are similar to those applied to other structural materials. Of course, the vector properties of slate differ greatly; thus, elasticity and crushing strength are great at right angles to cleavage. Extremes of heat or cold or a large amount of absorbed moisture reduce elasticity, transverse strength, and crushing strength.

Laboratory and field devices for measuring electrical resistance^{16,29,38} consist essentially of a current source and electrodes placed on opposite sides of the slab to be tested, the current being read by ammeter or voltmeter.

If structural slate is subjected over sufficiently long periods to highly corroding vapors or solutions, it may suffer color changes or partial disintegration. The most injurious agents are sulphurous, sulphuric, sulphuric-hydrochloric (mixed), hydrochloric, nitric and acetic acids, and sodium and ammonium hydroxides.⁶

SPECIFICATIONS

Roofing slate is sold in the United States by the "square," the slate necessary to cover 100 sq ft with a specified overlap—as a rule, 3 in. A similar unit, the mille, is used in Great Britain. The standard thickness is $\frac{3}{16}$ in. but greater thicknesses and irregular cleavage are sometimes desired for an "antique" appearance. Standard sizes for roofing slate in the United States range from 10 by 6 to 24 by 14 in. The order generally specifies color, and whether the entire slate must be free from dark beds ("clear") or have such dark beds beneath the overlap ("semi-clear") or exposed to view ("ribbon"). Certain thick and rusty-colored roofing slabs, designed to give an "antique" appearance, are especially sized and priced.

Millstock may not be too heavily "ribboned." The finish is specified; e.g., "sawed" or "split," "planed" or "honed." Dimensions and fittings are described.

Blackboards and bulletin boards, which are sold by the square foot, must be free from cracks, conspicuous beds, or other structural blemishes; they are preferably plane but may be slightly curved. The color must be dark gray or black. School slates may be framed before shipping. They must be smooth and dark. Dimensions are specified.

Electrical slate is sold by the square foot. It must be uniformly a poor conductor. Conductivity must be tested. The specifications include sizes.

For crushed slate, size is the prime consideration.

USES, MARKETING, AND PRICES

Uses—The following list briefly indicates the uses of slate:

- | | |
|----------------------------|-------------------------------------|
| 1. Roofing | 4. School slates |
| Standard roofing slate | Framed or unframed tablets |
| Slabs for "antique" roofs | Slate pencils |
| 2. Millstock | 5. Marbleized slate as a decorative |
| "Wallboard" for insulation | stone, for wainscoting, desk |
| Baseboard | fixtures, and so forth |
| Stair treads and risers | 6. Granules |
| Garden walks and flooring | Banded briquettes |
| Mantels | Surfacing flexible shingles |
| Sinks, dripboards, etc. | Surfacing roll roofing |
| Shower and toilet stalls | 7. Pulverized slate |
| Billiard table tops | Paint filler |
| Grave vaults and covers | Linoleum filler |
| Fence posts | Rubber filler |
| 3. Blackboards | Fuse covers |
| Blackboards | Substitute for fuller's earth |
| Bulletin boards | Pigment (if red or green) |
| | Abrasive soaps and polishes |

Marketing—Bowles⁵ points out that freight rates largely fix the market range of slate products; thus, in the United States the major part of the sales is confined to the area east of the Ohio drainage and hence near the quarries. Marketing centers are eastern Pennsylvania, New York City, Boston, Vermont, Richmond, and Norfolk. Structural and electrical slate may travel west to Chicago and St. Louis.

International trade is chiefly to and from coastal cities—Italian slate enters the eastern United States and British slate the coastal cities of Holland.

As building standards continue to rise in western United States and Canada, probably the frontier of slate will be pushed westward. Though in the United States slate is normally under severe competition from substitutes, the effect of World War II was to do away completely with any tendency to saturate the market in the first postwar years.

Prices—Quarrying fluctuates concurrently with changes in prices. Previous to World War I, the prices rose steadily. During the war they remained fairly constant, though production suffered through loss of labor. After the war came a distinct decline, culminating in 1929 to 1932, from which the slate industry, both abroad and at home, began a slow recovery. In World War II, labor and equipment for quarries and mills became unavailable. Immediately upon the war's end, demand became enormous and productive capacity in the United States is still nowhere near satisfying the market.

As prices vary greatly with the specific product and with time, few general statements can be made. Table 3 shows average sales values per unit in the United States for the principal slate products during recent years as given by the U. S. Bureau of Mines.

TABLE 3—Average Sales Value of Principal Slate Products in the United States

Year	Roofing Slate per Square	Mill Stock per Sq Ft	Granules per Ton
1943	\$ 8.75	\$0.35	\$8.71
1944	9.00	0.35	9.25
1945	9.64	0.35	8.80
1946	13.51	0.43	9.44
1947	18.14	0.57	9.96

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CHAPTER 44

NATURAL SODIUM CARBONATE AND SODIUM SULPHATE*

BY OLIVER C. RALSTON†

THE two chemical compounds, natural sodium carbonate and sodium sulphate, in their anhydrous condition are dealt in as "soda ash" and "salt cake"—names from an earlier day that are not as precise as the present accepted terminology. Once a large part of the sodium carbonate recovered was in the ash of seaweed, so it was logically called soda ash, and the corresponding potassium carbonate, once mainly recovered from wood ashes, was called potash. The term "salt cake" was applied to the sodium sulphate resulting from interaction of sodium chloride with sulphuric acid or sodium bisulphate, to form hydrogen chloride gas and an anhydrous cake of sodium sulphate. It was called "salt cake" and also "glassmaker's salt cake" because much of it was used in the production of glass.

The two salts occur in nature in a variety of forms, but whereas anhydrous sodium sulphate (thenardite) is fairly common, the anhydrous normal sodium carbonate, Na_2CO_3 , is almost never found in nature. The monohydrate (thermonatrite), $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, is seen occasionally, but it is never a major constituent in natural "soda" deposits. The high solubility of normal sodium carbonate is one reason for this. While both compounds occur widely in brines, the solid salts found in nature are usually trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) and thenardite (Na_2SO_4).

The natural brines containing workable quantities of the two sodium salts are largely found in the arid and semiarid portions of the western United States and other countries.

The classical discussion of the resources of these brines are those of Clarke,⁵ Chatard,⁴ Packard,¹⁹ Gale,¹¹ and Wells.²⁸ From North Dakota to California and from Arizona to the Canadian provinces of Alberta and Manitoba, saline lakes, dried-up lakes, playas, and similar land-locked depressions contain accumulations of saline matter. Sodium chloride is the predominant salt but some of the lakes contain predominantly either sodium carbonate or sodium sulphate. Often sodium carbonate

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† Chief, Metallurgical Division, Bureau of Mines, Washington, D. C.

and sodium sulphate are in nearly the same proportion and for this reason it is common to discuss them together.

As to the natural sodium compounds dealt in to any extent—sodium carbonate, sodium sulphate, and sodium borates—the last industrial census² shows that in 1939 this industry employed an average of 533 workers and used 16,066 horsepower. These products are heavy chemicals of relatively low value that compete with the synthetic chemical industry, in which sodium carbonate is made from common salt on a much larger scale and sodium sulphate is a by-product of a number of chemical industries. In localities of the eastern United States and Canada with humid climate, there are no natural deposits of sodium sulphate or carbonate, and these compounds are made from salt by the chemical industry. In the prairies and great plains, as one goes farther west and aridity increases, natural deposits appear and compete with the synthetic material from the eastern areas. The mountain states and provinces are more nearly self-sufficient, particularly in sodium sulphate, but only in 1947 has there been promise of anything approaching self-sufficiency in sodium carbonate products in the United States. Mexico has its inland arid belt and has begun to produce soda ash.

SODIUM CARBONATE

Soda ash has been in short supply, both in the United States and Canada, as this chapter was written, since fairly early in the second world war. An excellent discussion of the sodium carbonate industry at the beginning of the war was contributed by Harness and Coons,¹⁴ whose data show that in 1940 the total output of natural ash was 130,034 tons (short), whereas in 1945 it was over 180,000 tons. This compares with the United States total sodium carbonate production in 1944–45 of an average of about 3,750,000 short tons. The natural product therefore was inconsiderable as compared with the total output of the synthetic chemical industry; that is, 4.8 pct at that time.

Production of the natural salts, sodium carbonate and sodium sulphate, is given in Fig 1 from 1931 to 1947. Changes in future production of sodium carbonate are imminent. In 1947, the Permanente Metals Corporation³¹ added about 100 tons daily capacity at Owens Lake, California, the previous total output from that area having been about 30,000 tons a year, to supply soda ash for production of alumina in the Kaiser Bayer-process plant at Baton Rouge, Louisiana. Shortage in supply had prevented reopening of that alumina plant until the supply of soda ash from California was arranged.

A second influence on production is completion of a shaft to tap the trona deposits in Wyoming 13 miles west of Green River. In the very early days, a saline spring, high in sodium carbonate, at Green River had been used as a source of soda by the pioneers. Smith²⁵ has described

the development accomplished through drilling a bed of solid trona, about 99 pct pure and 12 to 20 ft thick, about 1500 to 1600 ft beneath the surface, originally shown by a wildcat oil well. The area circumscribed by five widely spaced holes is estimated to contain 300,000,000 tons of trona. The Westvaco Chlorine Products Co. completed a shaft during 1947 to exploit part of the deposit. Until a second opening into

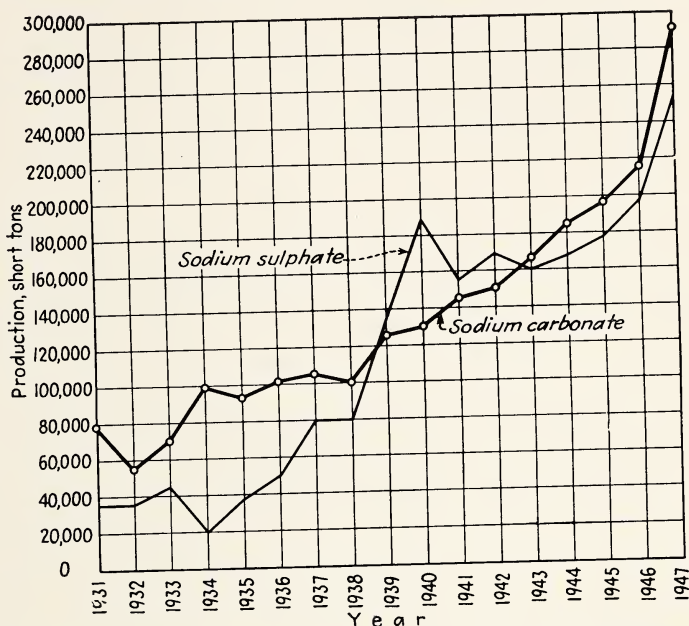


FIG 1—ANNUAL PRODUCTION OF NATURAL SODIUM SALTS IN THE UNITED STATES.

the deposit is completed, State law requires that the only mining done be in developing the necessary access openings, but there will be an increasing production from this unusual deposit of sodium sesquicarbonate. The shortage in supply in 1946 was about 500,000 tons, and it was expected to be alleviated very little during 1947–48, except from these sources.

At a depth of 300 ft in the salt body of Searles Lake, California, Foshag¹⁰ reports the finding of sodium bicarbonate, NaHCO_3 , in solid condition and in considerable quantity, which may be of much the same nature as the Wyoming trona beds. Immediate plans for production are not known to be in the making.

Forms of Sodium Carbonate

The normal carbonate (Na_2CO_3) contains 58 pct soda (Na_2O). This soda ash is known in light and heavy forms. If a hydrated form of sodium carbonate is calcined, the first product obtained is called light ash,

and weighs 32 to 35 lb per cubic foot. An extra light ash called "Fluf," which weighs 23 lb per cubic foot, is made at certain points in the drying and finishing, but it is not generally available in unlimited proportion. Dense ash results from calcination of the crude bicarbonate and comes in a medium-dense grade of 50 lb, or heavy-dense of 65 lb per cubic foot. The heavy grades are preferred for glassmaking.

Sodium Bicarbonate (NaHCO_3), or monosodium carbonate, is best known as baking soda. It is only slightly soluble in water in comparison with the normal carbonate and is therefore easily formed by precipitation from strong solutions of the normal carbonate by carbon dioxide gas. In turn, the bicarbonate precipitate, if heated, loses carbon dioxide and water vapor and leaves normal sodium carbonate as a residue. Besides its use as baking powder, it is widely employed as a mild alkali for medical, detergent, and chemical uses. It can be used in fire extinguishers, in ceramics, metal plating, and food preservation.

Trona, Sodium Sesquicarbonate ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) is the least soluble of the sodium carbonates and therefore most frequently found in nature. Soda ash, if left in air, tends to pick up carbon dioxide (CO_2) from the air and convert into trona. It is the first alkaline sodium excrement crystallizing from lakes containing alkaline sodium compounds. It was known as *urao* in ancient Egypt. The community named Trona, on Searles Lake, California, is named after this well-known mineral of sodium sesquicarbonate. The huge Wyoming deposit mentioned above, not yet fully delineated, is probably the residue of a large lake. How it could have formed in such pure form is difficult to explain. The only impurity present (1 pct) is the remains of eggs of *Artemia Salina*, a small crustacean, whose organic matter has also collected some iron compounds. When the Green River trona is calcined, the soda ash remaining is pinkish, owing to this iron.

The alkali playas found in depressions of the deserts consist of areas that are shallow lakes when there is any rainfall but that quickly dry up. Accumulation of saline matter washing in must be expected. The salinity is high in alkaline material when the terrain is volcanic, and much of the alkali is converted to trona by taking up CO_2 from the air. Most of these playas are not large enough to support commercial production for very long, if at all, but many of them have been used for local sources of alkali, as in the cyaniding of gold and silver ores in Nevada. This is economic only when lime can be burned and brought in at a higher cost than the trona in a playa can be scraped up.

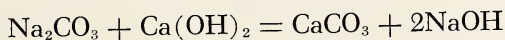
Sodium Carbonate Decahydrate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), known also as sal soda, washing crystals, washing soda, natron, and by other names, contains 63 pct water. Its cost is cheaper per pound than that of any other sodium carbonate product. It is also the most easily and quickly dissolved form of sodium carbonate, thus accounting for its popularity

in building up the necessary alkalinity for good detergency in washing fabrics. It melts at 34°C and loses excess water in air at temperatures below that, converting from a colorless crystal into a white powder containing less water of hydration. It is unusual in a natural state, except as an evanescent product.

Sodium Carbonate Monohydrate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) is given the mineralogical name of thermonatrite. It contains only 14.5 pct of water. It forms in rhombic crystals when a strong solution of sodium carbonate is cooled to 35°C or when crystals separate from a saturated boiling solution. It is used in manufacture of chemicals and for cleaning purposes; also in boiler compounds.

CAUSTIC SODA

Caustic soda (NaOH), or sodium hydroxide, is one of the main chemicals that can be made from soda ash. When a solution of Na_2CO_3 is treated with caustic lime ($\text{Ca}(\text{OH})_2$), the reaction that takes place is:



The reaction is reversible and approaches completion in the direction written only when solutions with less than 10 pct NaOH are made. The calcium carbonate is insoluble and can be filtered or settled out of the solution and the dilute solution of caustic soda then evaporated to the desired concentration.

Caustic soda has its greatest uses in making a wide variety of chemicals and in making rayon and cellulose film; next in order rank soap-making, alumina extraction, petroleum refining, pulp and papermaking, textile treatment and dyeing, rubber reclaiming, purification of vegetable oils, and a host of minor uses. With the war, the demand for aluminum sky-rocketed, and it now appears that at least part of the increased production is to be needed permanently. This means that in future the soda ash needed for the extraction of alumina will be a larger fraction of the total demand; it is causticized either before going into the process or during the extractive process.

Caustic soda is the strongest of the soda alkalies. It gives a pH of 14 when in water solution compared with 12.9 for normal sodium carbonate and 10.3 for sodium bicarbonate molar solution.

The glass industry is a huge consumer of soda ash. Glass commonly is a sodium-calcium silicate with a small quantity of alumina to decrease its solubility in water. The soda ash is the most expensive chemical ingredient in the glass. Water glass is a straight sodium silicate. With the shortage of tin for containers of all kinds, glass has filled the gap created by the tin shortage. The uses of glass also are increasing and are reflected in greater demand for soda ash.

The soap industry depends on forming sodium salts of fatty acids;

much of the soda used for this purpose is caustic soda, though part of it can enter the soap boiler as soda ash. Many special cleansers—for instance, the detergents for automatic milk-bottle-washing machines—are made up with various soda compounds.

Treatment of water is another heavy consumer of soda ash. Water contains calcium and magnesium compounds that contribute to hardness. Hard waters are softened by interaction of the dissolved calcium and magnesium and other heavy metal salts with soda ash and lime.

Soda pulp is one of the paper pulps made from wood by chemical means and is one of the important kinds. Rayon is made by the use of another sodium salt, which reacts with cotton fiber.

Metallurgical and chemical uses of soda ash are so varied that to describe each, even briefly, would require too much space.

Domestic Deposits of Soda Ash

As intimated in the foregoing paragraphs, natural sodium carbonate is found both in brines and in solid deposits. The Wyoming trona deposits are the largest known deposits of solid sodium carbonate in the world. The 300,000,000 tons delineated by five drill holes were all in thick beds, with no indications as to where the outer boundary of the deposit might be. One is justified in inferring that at least a billion tons is present. With the total national demand of the United States at about 4,000,000 tons per year, it is apparent that at the present rate there is enough soda ash for at least 100 years, and in greater probability for 300 years. In this estimate, no account is taken of the fact that, at a lower level, a second bed of trona about 6 ft thick was intersected in one of the drill holes.

At Searles Lake, the American Potash and Chemical Co., once called the American Trona Corporation, recovers sodium chloride, sodium carbonate, sodium sulphate, sodium tetraborate, sodium lithium phosphate, sodium bromide, and potassium chloride from the brine pumped from the interstices of the solid crystal mass that constitutes the main volume of the "lake."²¹ The bed of sodium bicarbonate mentioned by Foshag¹⁰ is below the level of the brine wells now being worked by this company. A competing company (West End Chemical Co.) draws brine from the salt mass of a different area, evaporates to discard some of the salt, and then passes the brine into carbonating towers where CO_2 gas precipitates a mixture of sodium bicarbonate and borax, which is separated later into the individual salts.

Owens Lake, Inyo County, California, has been worked for soda since 1885. It is well documented by Harness and Coons¹⁴ and by Dubs.⁹ Originally it was a landlocked lake of Brackish character, fed by freshwater streams. Diversion of the streams to the Los Angeles water system

permitted the salty lake to dry up, like Searles Lake, and become a mass of solid crystals and mud with a strong brine standing in the interstices. This forced a change in the technology of extraction of the sodium salts. At present, the crystal mass, 7 to 9 ft deep, is trenched and the brine is drained from it to pumps that move it to evaporating ponds of three different operators, for removal of sodium chloride up to the point where the more valuable sodium salts begin to crystallize. Carbonation, as in the West End plant at Searles, is one of the practices used for separating the mixture of sodium salts. It was on this lake that the Permanente plant was erected in the short space of 35 days in 1947, to supply soda ash for the Baton Rouge alumina plant.

Sporadic attempts have been made to work the many smaller lakes in the other arid states. Nevada has records back in the early days of small use of playa trona and so does Wyoming. Just before the war, the Sodium Products Co., of Spokane, Washington,¹⁶ had a small plant at Wilson Creek, 100 miles west of Spokane, in a 13-acre lake between lava cliffs, with wells drilled into the mixed silt and sodium carbonate to a depth of 50 ft. Steam and water were used to make a solution, the silt was settled and filtered out, and the hot solution was allowed to cool and crystallize. The enterprise is said to have ceased before the war.

Small lakes in Wyoming form a string from southwest of Laramie to north of Rawlins and have produced sodium carbonate and sodium sulphate. In the early days, the sodium carbonate was desired. In recent years, sodium sulphate has been produced for cattle tonic in Wyoming and adjacent eastern states. Some of the lakes have magnesium sulphate as well as sodium sulphate, but there no sodium carbonate can exist in the water. The lakes are either of the sodium sulphate-sodium carbonate type or of the sodium sulphate-magnesium sulphate character.

The lake in Mexico valley on which the Aztec capitol was built has been lowered by drainage and has almost disappeared. The lands now have 6800 miles of subsurface drains to reclaim the resulting alkali lands. These drains center to a spiral evaporating pond on Lake Tescoco, described by Gerstel.¹³ The spiral pond is called the Caracol (snail), and the alkali water starts evaporating in the outer whorl, which is of the greatest area, flowing as it decreases in volume along the spiral toward the center, from which it is pumped to crystallizers. The Caracol covers 2025 acres, with an annual solar evaporating capacity of 10 million tons of water (there are 78 in. annual evaporation and 27 in. rainfall, or a net evaporation of 51 in.). At the center, the water carries 300 kg salts per cubic meter and has been in the system one year. The crystallizers are also solar. The crude crystals are treated at Netzahualcoytl. Annual capacity is rated 50,000 tons NaCl, 20,000 tons NaOH, 13,000 tons Na_2CO_3 , 2000 tons Na_2SO_4 , 6000 tons KCl and 2600 tons $\text{Na}_2\text{B}_4\text{O}_7$. This interesting experiment should be watched.

Tariffs and Prices

Harness and Coons have tabulated the history of tariffs as shown in Table 1. A spot history of prices since 1925 is also from the Bureau of Labor Statistics, Department of Labor, as quoted by Harness and Coons in Table 2.¹⁴

SODIUM SULPHATE

Natural sodium sulphate is only a small fraction of the total "salt cake" used in the United States and Canada. For instance, in 1931 the natural sodium sulphate produced in the United States was about 35,000 tons, while the total consumption of natural and synthetic in the same year was about 120,000 tons. Most of that synthetic came from Germany as a by-product from the muriatic acid and magnesium industries. When World War II cut off the German salt cake, increased production of both natural and synthetic was encouraged. The chart of United States production (Fig 1) shows this increase, but part of it was due to overall increase in general demand resulting from our own war activity.

The largest increase in synthetic chemical salt cake was by Bay Chemical Co., of New Orleans, with plant at Weeks, Louisiana, using salt from the salt mines of Louisiana and sulphur from its salt-sulphur domes to make hydrochloric acid and salt cake. This was done in a modernized Hargreaves process fully described by Alfred Lippman, Jr., and R. L. Comstock¹⁷ in an unusually informative patent specification. The sodium sulphate was needed for the kraft-paper mills of the southeastern states; the hydrochloric acid was used for a variety of purposes, an important one being the removal of iron, calcium, and other metal carbonates associated with Bolivian tin ores smelted in East Texas.

The greatest increases in production of natural sodium sulphate took place in California. The huge plant of American Potash and Chemical Co. at Trona, on Searles Lake, increased its output to the full amount of sodium sulphate in the brine treated by the plant. Most of the sodium sulphate forms a double salt, $\text{Na}_2\text{CO}_3 \cdot \text{Na}_2\text{SO}_4$, called "burkeite" in this plant, and the double salt is separated from the brine and then into sodium carbonate and sodium sulphate.

Dale Lake, a dry lake 200 miles east of Los Angeles, was also brought into production, and described by Manning,¹⁸ and the operation will be described later in this article. Shipments were resumed from the Bertram deposit in Imperial County, California, as described by Sampson and Tucker,²² of the California Bureau of Mines.

Mineral Forms of Sodium Sulphate

Thenardite (Na_2SO_4), the anhydrous form of sodium sulphate, is the usual form found in beds of buried sodium sulphate. Temperatures

TABLE 1—*Tariffs (Harness and Coons¹⁴)*

Soda Ash				Sodium Bicarbonate		Sal Soda	
Date of Act	Tariff, Cent per Lb	Date of Act	Tariff, Cent per Lb	Date of Act	Tariff, Cent per Lb	Date of Act	Tariff, Cent per Lb
1883	$\frac{1}{4}$	1913	Free	1883	$1\frac{1}{2}$	1883	$\frac{1}{4}$
1897	$\frac{3}{8}$	1922	$\frac{1}{4}$	1913	$\frac{1}{2}$	1894	$\frac{1}{8}$
1909	$\frac{1}{4}$	1930	$\frac{1}{4}$	1930	Free	1930	$\frac{1}{4}$

TABLE 2—*Annual Average of Wholesale Price Quotations per 100 Pounds of 58 Per Cent Na₂O Light Ash¹⁴*

Year	Average Price at Works, Chemical Soda Ash	Year	Average Price at Works, Chemical Soda Ash
1925	\$1.430	1934	\$1.230
1926	1.430	1935	1.230
1927	1.375	1936	1.23
1928	1.366	1937	1.157
1929	1.345	1938	1.050
1930	1.345	1939	1.050
1931	1.161	1940	1.050
1932	1.182	1941	1.050
1933	1.197	1945	1.10
		1946	1.20

above 32.4° C, or earth pressure, seem to alter the more hydrous forms into thenardite. When a brine containing sodium sulphate is evaporated at temperatures below 32.4°C, the more hydrous form "mirabilite" (Na₂SO₄·10H₂O), also called glauher's salt, and sodium sulphate decahydrate crystallize. "Glauberite" should not be confused with "glauher's salt," being a double sodium-calcium sulphate (Na₂SO₄·CaSO₄), of which there is a fair-sized deposit in southern Nevada. The mineral burkeite (Na₂CO₃·Na₂SO₄), another double salt, has already been mentioned. It tends to form when brines containing both sodium carbonate and sodium sulphate are fractionally crystallized.

The simplest mining operation in this field is the digging of solid thenardite from thick beds, which is sold after little or no cleaning. If sodium sulphate is won from natural brines, the halurgist (salt worker, like metallurgist, metal worker) is confronted with the refractory behavior of mirabilite and burkeite most frequently.

Uses of Sodium Sulphate

Glass is a sodium-calcium silicate, usually made with soda ash as the source of soda (Na₂O). Sodium sulphate is a cheaper supplier of soda and its sulphate radical decomposes into gaseous oxides of sulphur

and oxygen and leaves the furnace. Weyl²⁹ has discussed quite thoroughly the use of sodium sulphate as a source of soda in glass. Salt cake, the anhydrous form of sodium sulphate, is desired by the glassmakers. It requires a higher temperature for the silica of the glass batch to decompose it than does soda ash. Its alkali and oxygen become available to the batch in the last stages of melting, at which time they are wanted for fining and oxidizing, and as a remedy against scum. Excessive use of sulphate injures the furnace refractories. Fining efficiency is at an optimum, with $\frac{1}{20}$ of the alkali entering the batch as Na_2SO_4 . However, up to half the alkali of a glass batch can enter as sulphate.

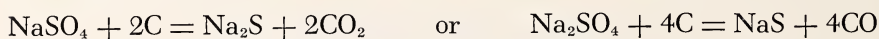
TABLE 3—*Annual Average Prices at Mine of Natural Sodium Salts per Short Ton^a*

Year	Sodium Sulphate	Sodium Carbonates
1929	\$?	\$18.62
1933	5.25	13.03
1937	7.42	11.38
1940	8.18	12.53
1942	9.86	14.30
1943	9.68	15.32
1944	9.34	15.50
1945	8.58	15.62
1946	8.04	15.90
1947	12.93	20.00

^a From Minerals Yearbook, 1946, U. S. Bureau of Mines.

Perhaps the largest and most important use of sodium sulphate is in the making of kraft (wrapping) paper. Much of this is manufactured from the soft pines of the southeastern states. Hence, the Louisiana-Alabama-Florida area provides an important marketing center. Sodium sulphate is reduced to sodium sulphide by heating with a reducing agent, like wood waste, and the sodium sulphide (Na_2S) in a solution of suitable strength is of the right alkalinity for cooking wood fiber to give a strong paper stock. It is re-used repeatedly, but losses must be made up. The subject is discussed by Martin Williams,³⁰ who says that a ton of kraft paper requires 1.32 cords of wood and 360 lb of new sodium sulphate. In 1938, there were produced in the United States 2,452,076 tons of kraft paper requiring 440,000 tons of sodium sulphate.

Sodium sulphate is reduced to sodium sulphide by carbon, hydrogen or hydrocarbons at temperatures above 950°C , and preferably above its melting point. The reaction with carbon is illustrative:



Much of the commercial sodium sulphide used in the chemical and metallurgical industry, as in the paper pulp described (known as sul-

phate-process pulp) was originally made in giant rotating horizontal cylinders filled with coke and heated above the melting points of Na_2SO_4 and Na_2S by a flame passing through the cylinder. On quenching in water, the mass permitted the sodium sulphide to be dissolved. Such sodium sulphide was also accompanied by sodium thiosulphate, which had to be separately crystallized. Either a reverberatory or a blast furnace can be used for the same purpose. If reduced in an electric furnace, no other sulphur-oxygen complexes like the thiosulphates are formed and pure molten sodium sulphide can be tapped directly into molds or drums with exclusion of air. Sodium sulphide has a multitude of uses. In the mineral industries, it is used in nickel refining; in flotation, for sulphidization of oxidized ores of lead, copper and silver; in hydrometallurgy, for treatment of antimony and other minerals.

As a mild laxative, sodium sulphate is more commonly used for cattle than for human beings, its cheapness being important, and it is often spoken of as a stock tonic. The solid deposits and the brines in Wyoming are sent to adjacent states where cattle feeding is an important industry.

In the dye industry, sodium sulphate is put into the baths of acid colors for wool or cotton to the extent of 20 pct of the weight of the goods to be dyed. A more level and better distribution of the dye is claimed. It also benefits the curing of hides in the tanning industry.

In chemical or metallurgical processes that require both sulphuric acid and caustic soda, and where a sodium sulphate waste product is formed, the electrolysis of solutions of sodium sulphate to recover both the acid and the alkali as dilute solutions, with simultaneous generation of hydrogen at the cathode and oxygen at the anode, can be considered a means of keeping these two chemicals in closed cyclic operation. Their dilute solutions may have to be concentrated before they are usable in the process and thus render such a cyclic recovery less desirable economically. However, if the sodium is collected in a mercury cathode, the amalgam can be contacted with just enough steam to make a very concentrated caustic soda, thus escaping the evaporation of dilute caustic soda, but the dilute sulphuric acid formed at the anode of such an electrolytic cell cannot be so easily avoided.

Sodium sulphate is added to some electroplating baths to increase their conductivity and in this case it must be of high purity.

Technology (Halurgy) of Natural Sodium Sulphate

Beds of pure, solid, sodium sulphates are rare and when mined precautions are necessary to prevent contamination. The solid deposits usually have unacceptable amounts of both soluble and insoluble impurities. Earth or mud, sand, gypsum, calcite, dolomite, magnesite, and other materials are often present and must be avoided as much as possi-

ble during mining or removed from the broken mined material by hand, by washing, or by various mineral-dressing procedures.

An example of such an operation was the thenardite deposit mined at Camp Verde, Arizona, for many years. The horizontal bed was capped with one foot of solid sodium chloride. This was left during mining to afford a good roof to prevent slumping of the loosely consolidated clays and sands above and to prevent mixing of the salt with the thenardite. When the miners were ready to let the roof fall in a mined-out room, the halite was removed quickly from the roof and the room left for a gradual cave-in to ensue. The thenardite was crushed by toothed rolls to about one-inch diameter and washed in a rotating trommel screen with saturated sodium sulphate solution returned from the tailing pond, and finally with a small amount of fresh water. The brine washed away clay and other powdered minerals, to settle in the pond; the fresh water tended to dissolve NaCl first and leave the sodium sulphate. The trommel had a screen of 4-mesh opening, and sodium sulphate fines went to the tailing pond with the waste. Any lumps of gypsum in the coarse sodium sulphate remained with it. The drying of the washed anhydrous Na_2SO_4 was done at a temperature (above 130°C) that would cause calcination and decrepitation of the gypsum. Therefore, part of the plaster of paris dust formed from the latter floated off in the drier gases, and when the dried hot product was screened most of the remaining gypsum went into the fines. These screened fines were 80 pct Na_2SO_4 and only 20 pct CaSO_4 but were stock-piled during the life of the plant and never were used, for lack of a suitable process for treating them. The finished product shipped to the paper mills contained 2 to 5 pct NaCl but only the material with 1 or 1.5 pct NaCl would be accepted by the glassmelters.

During operation of the deposit at Rhodes Marsh, near Mina, Nevada, both solid thenardite and loose or partly dehydrated glauber's salt were mined. The desert air tended to dry out the glauber's salt resulting from evaporation of solutions formed during rains and collecting in the lowest point of the playa. The same is true in the "lakes" of Wyoming, Saskatchewan, and Alberta. If reliable solar evaporation could be carried out without interruption by rain, it would be inexpensive to install and operate a scheme for: (1) the dissolution of sodium sulphate in water; (2) crystallization of glauber's salt by solar evaporation; (3) draining off of mother liquors and impurities; and (4) solar drying of the glauber's salt to leave partly or completely dehydrated sodium sulphate. Owing to its unprotected outdoor nature, this process cannot exclude sand and dust blown in by wind, and it is usually difficult to exclude intrusion of drainage water, with suspended mud and other impurities. It is, therefore, not a common practice. The Wyoming sodium sulphate intended for use as a cattle tonic need not be free of

NaCl or insoluble silt or mud. The requirements of the consumer are the ruling factor with respect to the possibility of using this simple technology. Both crude and refined products are capable of finding certain markets.

Sodium Sulphate from Brine

The source of much sodium sulphate is either a brine or a deposit from which a brine can be prepared. The various lakes listed as sources have brines with varying proportions of sodium sulphate, chloride, carbonate, bicarbonate, or borate, and also in solution potassium, calcium, magnesium, and occasionally minor amounts of other cations. Such brines, if dilute, can be concentrated by evaporation. The outstanding fact used in sodium sulphate halurgy is its high rate of increase of solubility with rise of temperature, or the converse—the decrease in solubility with drop of temperature. In water, the solubility is only 5 grams per 100 grams of water at about 0°C but rises to 50 grams Na_2SO_4 per 100 grams water at 33°C, the melting point of glauher's salt. Merely refrigerating the strong brine causes most of the sodium sulphate to crystallize out as the mineral mirabilite, also known as glauher's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), a crystal that consists of nearly 56 pct water by weight. If the brine contains other sodium salts, particularly NaCl, the solubility of glauher's salt at low temperature is further lowered; hence greater recovery can be obtained by the refrigeration technique. The crystals can be separated by centrifuging and cleaned by washing on the centrifuge. The same crystals can be obtained by continued evaporation of brines containing sodium sulphate at any temperature below 33°C; hence mainly solar evaporation. The significance of the temperature 33°C is the fact that glauher's salt melts at this temperature and if water evaporates from the melt at any higher temperature it leaves a crust of sodium sulphate in anhydrous condition. The solubility-temperature curve of Na_2SO_4 (anh.) in water begins at 33°C and has been traced to temperatures as high as 350°C in high-pressure autoclaves by Schroeder, Gabriel, and Partridge.²³ At 33°C, it is about 50 grams Na_2SO_4 per 100 grams H_2O . With rise of temperature, it falls off to a minimum of about 41.5 grams at 120°C, climbs to a maximum of 47 grams at 250°C, then falls to 2 grams at 340°C, the highest temperature yet used. The solubility decrease with lower temperature is widely used, but the newly discovered decrease between 250° and 350°C is as yet unused.

The simple solar evaporation of sodium sulphate brines as practiced by a number of the Canadian enterprises is described by Cole⁶ in connection with seasonal evaporation taking place in the summer months. In the late summer, the brines are sufficiently saturated so that a slight drop in the temperature causes crystallization of mirabilite, and continuation of the process through the fall builds up a bed from a few inches to

2 ft deep, and quite clean. A certain quantity of glauher's salt can be shipped as such and is harvested with shovels, washed free of brine, and sacked. The remainder must be converted to salt cake and is not harvested until the deposit is consolidated enough to support wagons or trucks. The crystals are loosened by plows, scraped into windrows, and then hauled to stock piles on the shore for dehydration.

On the Great Salt Lake and many of the lesser lakes, the chilling of the brine in winter often causes separation of mirabilite crystals, called in this case "winter salt," which either sink to the bottom or are carried by winds and currents to the shore, piling up under favorable conditions to a depth of a foot or more. Sporadic collection of winter salt has been attempted (Wells²⁸) but the phenomenon has not been used so much by man as by nature. The crystals migrate down into the sands by dissolution and recrystallization and finally are protected by the sand cover from removal by warmer waters, thus giving rise to the huge accumulations of mirabilite under or adjacent to brine lakes, which have been little studied up to the present. Zdanovskii et al³¹ have made a report on the deposition of 40,000,000 tons of winter salt each season on Anzh-Bulat Lake in Russia. Near Monahans, Texas, the Ozark Chemical Co. has operated since 1933, leaching a deposit of natural sodium sulphate with a salt brine pumped from a deep well penetrating the Permian age salt beds; this brine, saturated with sodium sulphate, is chilled in a heat exchanger by refrigerating machinery. The presence of the sodium chloride in the brine causes a more effective crystallization of mirabilite than from a straight water solution, and the crystals are separated from the brine, which is returned to leaching. If the mirabilite is to be sold direct as glauher's salt, the crystals are washed free of sodium chloride brine before draining and drying free of hygroscopic moisture. Refrigeration of sodium sulphate from saline solutions in similar manner has long been practiced in Europe. As an instance, the liquors leached from a chloride-roasted pyrite cinder at Duisberg K  pferr  tte, Duisberg, Germany, are refrigerated for this purpose to get an additional salable product, normally wasted in a metallurgical plant.

Dehydration of Mirabilite

The most serious technical problem in sodium sulphate halurgy is that of dehydrating mirabilite or glauher's salt. The melting point of the crystals of sodium sulphate decahydrate, containing 56 pct water, is 33  C, the critical point in the whole series of solutions of sodium sulphate. From the melt, on evaporation of water, anhydrous Na_2SO_4 is deposited, not in easily handled clean crystals but as an adherent, stony accretion on the walls of the apparatus. The decahydrate can be air-dried below 33  C and will yield a loose white powder at anhydrous Na_2SO_4 , but any attempt to accelerate drying by heating results in melting at

33°C and mechanical difficulties thereafter in separation of the desired anhydrous salt cake.

A review of methods of dehydrating mirabilite before 1935 is given by Tyler.²⁶ A considerable increase in information on other new developments in dehydration since then is available but few seem to offer any further improvement over submerged combustion. Two different multistep dehydrating processes were reported respectively by Conley and Partridge,⁷ of the Bureau of Mines, and by Pierce,²⁰ of Horseshoe Lake Mining Co., Ormiston, Saskatchewan, a plant owned by International Nickel Co., which supplies the sodium sulphate for the Orford process of treating nickel-copper matte.

The most successful method yet devised for dehydrating mirabilite is that of the Ozark Chemical Co. Mirabilite is melted in its water of crystallization and then heated by submerged combustion, as described and patented by Douglass and Anderson.⁸⁴ This type of evaporator is also described by Schultz and Lavine.¹⁵

The molten mirabilite is heated and evaporated by submerging the nose of a large gas burner directed downward into it. The barrel of the burner is large enough to permit complete combustion before the hot gases force their way from the lower end of it and rise through the fusion, carrying off moisture. A mush of anhydrous Na_2SO_4 suspended in molten $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ is formed and this mixture is passed continuously through Bird centrifuges, which separate the anhydrous salt, still slightly wetted by molten mirabilite, and return the molten mirabilite to the evaporator. The salt cake is passed through ordinary rotary cylindrical driers to remove the moisture in the film of mirabilite on the particles of anhydrous salt and is then sacked in the anhydrous form for sale as salt cake.

Deposits of Sodium Sulphate

Cole⁶ believes that the largest deposit of glauber's salt in the world is in Canada. He says that the chain of lakes in Saskatchewan (23) and Alberta (2), as shown by incomplete data, must contain 115 million tons of hydrous sodium sulphate.

The writer holds the opinion that a proper investigation of the bottom and shores of the present Great Salt Lake and the dry salt beds west of the lake to Wendover, Utah, will show a much greater tonnage of mirabilite. The traditional descriptions of sodium sulphate around the lake refer only to the southeastern shore and southern end—the most convenient places where access is to be had. The bottom of the lake is made up of oölites of calcium carbonate to unknown depths. The strong sodium chloride brine occupies the interstices between the oölites for the top few feet, but below that and to unknown depths the oölites are in a matrix of mirabilite resulting from the segregation of "winter salt"

during the winter season. At the northern end of the lake, the Lucin cutoff of the Southern Pacific Railroad is built on piles driven into the bottom of the lake, and stories of the difficulty of driving the piles into the "soda" on the bottom attest the presence of the mirabilite matrix for the oölitic sand. The railroad engineers were baffled until the nature of the matrix was learned, and the problem was solved by driving a small pipe supplied with steam into the sand ahead of the pile. The mirabilite had to be heated only to 33°C to liquefy and allow the pile to be driven into the warm sand. Drillings of the salt desert also show high amounts of mirabilite.

Further doubt as to Cole's estimate that western Canada has the greatest deposit of mirabilite in the world is entertained by the writer as more information is acquired about the salinity of the lakes in the closed basins of southeast Russia and southwest Siberia.³¹ This area promises to become the one with the greatest known reserves of sodium sulphate. Chile has sodium sulphate in playa lakes and in sodium nitrate deposits, having shipped sulphate from both.

UNITED STATES

The domestic deposits have been summarized by many authors; Cole,⁶ Tyler,²⁶ and the U. S. Tariff Commission¹ among others. The more important states with respect to sodium sulphate deposits and production are listed alphabetically herewith in brief form:

Arizona—The Camp Verde deposit in Yavapai County was worked by prehistoric Indians for the sodium chloride that makes up the upper foot of this deposit and doubtless utilized some of the thenardite for its purging properties. It was last worked by American Cyanamid Co. under the name "Arizona Chemical Co." about 1934. The more accessible portion had been mined from the deposit, then an increased freight rate was exacted, and heavy competition in California forced moving of operations to Texas. The deposit is about 4½ ft thick and is thought to have originated in a Tertiary lake that once occupied that part of the Verde River Valley.

California—At Trona, on Searles Lake, the American Potash and Chemical Co. has been a consistent and growing producer of sodium sulphate products from the brines and the solid material in the lake, principally mirabilite from the brine and thenardite in the solid salts. The Soda Lake on the Carisso Plain in San Luis Obispo County has shipped important quantities of mirabilite from McKittrick. A thenardite-bloedite deposit (called the Bertram) has been worked intermittently in Imperial County (Sampson and Tucker²²). When Germany was prevented by war from shipping salt cake to the United States, many of the desert lakes in California were restudied. The largest de-

velopment of this kind, by Dale Chemical Co., was at Dale Lake, 150 miles east of Los Angeles, described by Manning¹⁸ as having broken ground in 1940 and developed to produce 50,000 tons of sodium sulphate per annum by solar evaporation of brines. It is stated that test wells on a 520-acre tract show 12,000,000 tons of sodium sulphate, and that the total reserves in the entire 1500-acre property are estimated at 35,000,000 tons.¹⁸ A subterranean brine contains 22.5 pct NaCl and 7.5 pct Na_2SO_4 . Production starts in the winter months by freezing out the sodium sulphate as winter salt, causing deposition of glauber's salt below 60°F. Residual NaCl brine is pumped to a suitable solar evaporating pond for production of salt. The glauber's salt is redissolved in fresh water and exposed in shallow ponds lined with wood. When summer temperature rises above 70°C, anhydrous Na_2SO_4 , 99.5 pct pure, settles out.

Colorado and Idaho have had no further developments of their small deposits since Tyler wrote.

Nevada—The principal producer in recent years in Nevada has been Rhodes Marsh, near Mina, Mineral County. It has an area of 11 square miles but has been worked mainly for a 3 to 5-ft bed near the middle, containing mainly thenardite. It is not active at present. In Clark County, a deposit of glauberite, a double sulphate of calcium and sodium, not ordinarily an industrial mineral, is largely covered by the water of Lake Meade, above Hoover Dam, and is the subject of a damage suit against the Government.

New Mexico—Whereas previous summaries have shown sodium sulphate in Dona Ana County, New Mexico, near the White Sand deposits of gypsum sands, brines have been discovered west of the Pecos River near the potash mines; 34 to 45 pct of the total salinity is Na_2SO_4 and the remainder mainly magnesium and potassium sulphates, with minor quantities of magnesium chloride and borate. They are thought to be associated with the potash beds, perhaps being the material extracted in modern "solution channels" that have developed since the beds were deposited, and through which part of the deposits has disappeared.

North Dakota—In the northwest corner of the state, near Grenora, in line with corresponding lakes in Saskatchewan, the Federal Emergency Relief Administration in 1934 investigated the tonnages and grades of seven lakes containing sodium sulphate. A brief report by Lavine and Feinstein¹⁵ shows that in most of the lakes the sodium sulphate content of the saline matter was about 94 pct, with magnesium sulphate, calcium sulphate, and sodium chloride as the main impurities, in the order named but differing in ratio. The gross tonnage of the seven lakes was about 23,000,000 tons of glauber's salt, or about 10,000,000 tons of Na_2SO_4 .

Oregon—There is nothing new to add to the information about deposits in Oregon compiled by Tyler. The lake deposits are small and are badly mixed in chemical character.

Texas—Besides the deposits being worked by the Ozark Chemical Co. operating 11 miles south of Monahans, Texas, is the lake of 120 acres consisting mainly of glauber's salt. North of it, in the Texas Panhandle area, are two more deposits, developed by Arizona Chemical Co. after the mine at Camp Verde, Arizona, was shut down. One of these is at Brownfield, the other at O'Donnell. The sodium sulphate is a solid bedded deposit dissolved by pumping in water through drill holes. The issuing solution is chilled by spraying in the desert air to about 50°F, causing glauber's salt to be crystallized out.

Utah—The important information on Utah is at the beginning of this section on deposits. Utah could become an important producer of sodium sulphate, except that most of the market for it is about as far by rail as could be found in any of the United States.

Washington—Tyler²⁶ lists the location of the deposits, most of which are small. Omak Lake, Soap Lake, Monse dry lakes and others have been the sites for a number of enterprises. Actual commercial production has been small. Not much kraft-paper pulp is made in Washington but with a good supply of sodium sulphate there is no reason why there could not be a bigger production.

Wyoming—The enterprises in Wyoming, briefly reviewed earlier in this chapter, are in a chain of lakes from the Colorado border south of Laramie to 30 miles north of Casper, most of them playas with solid salts available but with brine also available at least part of the year. In some of these lakes, as in the Canadian lakes in Saskatchewan farther north, a considerable quantity of magnesium sulphate accompanies the sodium sulphate. Some of them have no magnesium at all but instead are alkaline with sodium carbonate. Laramie, Albany, Natrona, and Carbon Counties have these lakes. Minor lakes are in Sweetwater, Fremont, and Johnson Counties. Some have been worked for cattle tonic since 1892. Waters carrying sodium carbonate and sodium sulphate are mainly in Natrona County. Those carrying magnesium sulphate and sodium sulphate are mainly in Albany County. Those containing mainly sodium sulphate with 3 to 9 pct magnesium sulphate are in Carbon County. Gross tonnages are relatively small.

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CHAPTER 45

SPECIAL SANDS

BY H. RIES*

SPECIAL sands are those that are employed for special purposes. They have a limited use, as compared with sands for concrete and plaster. The sands discussed in this chapter are those used for foundry purposes, glass manufacture, filter beds, abrasive purposes, sandblasting, engine sand, sand for sheet asphalt, and furnace sand. These sands are almost invariably high in silica, consisting chiefly of quartz grains. In some—for instance, glass sands—freedom from ingredients other than silica, such as iron oxide, is important. Certain grades, like filter sand, require rather careful sizing, and in foundry sands the bond, usually clay, is important.

One deposit may sometimes be used to supply several grades or types of sand by appropriate methods of screening and washing. The special sands discussed here are usually obtained from deposits of unconsolidated material but sands high in silica are derived occasionally from soft sandstones that can be disintegrated easily. Requirements are not the same for all uses, and, while certain properties may be demanded, there are no officially adopted standard tests except for foundry sands.

FOUNDRY SANDS

Definition—Foundry sands include those siliceous sands that are used to make the forms for casting metals. If these are employed for making molds, they are known as molding sands; if for the cores that form the hollow spaces in the casting, they are called core sands.

Naturally bonded sands are those containing a variable, though not usually large, amount of clay, which serves as a bond. Synthetic sands, now much used, represent an artificial mixture of sand with usually fire clay or bentonite. Core sands may be bonded with oil, cereal binders, resin, pitch, or other materials. The foundrymen apply the term “sharp sand” to one that is free from bond.

Properties—The important properties to be tested at room temperature are texture or fineness, permeability, strength, deformation, and flowability. Those tested at elevated temperatures are compressive strength, expansion and contraction, sintering point, and durability.

More attention probably has been given to research on the properties

* Professor of Geology, Emeritus, Cornell University, Ithaca, N. Y.

of foundry sands and the development of standard methods of testing them than to any other special sands.^{1,2}

Character of Grains—The grains of a foundry sand range from about 3 mm in diameter to particles small enough to be called clay. The sand grains usually are subangular to angular, rounded grains being rare and occurring mostly in sizes coarser than 60 mesh.¹⁷ The surface of the grains may be smooth or rough, clean or stained. Some sands contain compound grains.

Fineness—The term “fineness” refers to the size of the grains. The American Foundrymen’s Association* classes as “clay” material finer than 20 microns, and refers to larger sizes as “grain.”¹⁷ Sands in which large grains predominate are called coarse, while those with a predominance of small grains are called fine. The fineness of a sand is expressed by the “grain-fineness number,” which represents approximately the number of mesh per inch of the sieve that would just pass the sample if its grains were of a uniform size.² The American Foundrymen’s Association divides sands into different classes, based on the grain-fineness number and the percentage of clay.² The fineness of the sand exerts an influence on the permeability and strength, as well as the smoothness of the casting. Table 1 shows the variation in texture of a range of sands and their other properties for the corresponding grades.

Unfired Strength—Unfired strength may mean the strength of the sand in its green (still containing moisture) or dried condition, and this may be tested in terms of compression, tension, or shear. The compressive strength is tested more often than the other two. Other things being equal, the green strength depends largely on the amount and kind of clay present. The amount of moisture also affects the green strength. It causes it to rise as more is added until the optimum strength is reached, after which the continued addition of moisture causes it to decline.

Dry strength, however, increases with the moisture content of the sand (Fig 1).

Flowability—The term “flowability” refers to the property of the sand that permits it to enter all parts of the mold when rammed.

Deformation—“Deformation” describes the change in linear dimension of a sand mixture that accompanies a stress.¹⁷ It is used for calculating the sand-toughness number, which indicates the workability of the mixture. Table 2 gives the green properties of some sands.

Tests at Elevated Temperatures—Tests at elevated temperatures are made usually at 1000°F or higher. They may include the hot compressive strength, expansion and contraction, collapsibility applied especially to core sands,² and sintering tests. In addition, it has been suggested by Caine that test specimens may be plunged into hot metal or exposed directly to its heat.

* The name is now American Foundrymen’s Society.

TABLE 1—Sieve Tests and Other Properties of a Series of Sands

Grade of Sand	Percentage Retained											AFA Fines-ness Figure	AFA Per-meability	Green Shear Strength, Psi	Green Com-pres-sion, Psi		
	6	12	20	30	40	50	70	100	140	200	270					Pan	Clay
Albany:																	
00.....		0.02	0.02	0.04	0.04	0.06	0.16	0.74	2.36	12.12	16.30	54.44	13.68	250	7.2	2.0	7.4
0.....			0.04	0.08	0.10	0.12	0.48	4.18	8.20	21.48	18.94	33.68	12.50	207	11	1.6	5.6
1.....		0.02	0.04	0.10	0.24	0.94	3.14	9.50	14.92	23.60	13.28	23.24	10.98	172	14	1.6	5.6
1½.....		0.05	0.14	0.25	0.73	2.79	8.16	15.76	17.28	20.06	9.10	14.34	11.34	139	17	1.5	5.6
2.....			0.06	0.20	1.54	11.04	20.64	20.76	9.54	7.70	3.72	9.34	15.46	101	31	1.8	6.1
2½.....	0.02		0.10	0.14	2.28	13.80	21.92	22.10	10.44	7.48	3.36	6.68	11.66	86	53	1.6	5.6
3.....		0.18	0.44	2.14	9.46	19.92	24.60	16.40	4.80	3.94	1.96	5.10	11.06	73	96	1.0	4.4
3½.....		0.12	1.04	6.14	14.58	30.54	18.32	13.32	4.84	5.64	1.96	4.38	10.72	67	142	1.1	4.2
4.....	0.18	1.06	3.22	3.24	15.20	29.84	20.52	5.62	1.42	1.50	0.90	4.40	10.90	57	178	1.0	4.2
Millville gravel....	6.4	12.2	20.0	14.4	14.0	10.0	5.0	2.6	0.8	0.4	0.2	0.8	13.2	26	650	3.7	16.5

Permeability—Permeability is the physical property of the sand that permits the passage of gases. Upon this property of permeability, depend the venting qualities of sand molds and cores. The permeability is determined by measuring the rate of flow of air through a standard specimen of sand under a given pressure. Fine sands have a low permeability while coarse ones are more permeable (Table 1). Clay decreases

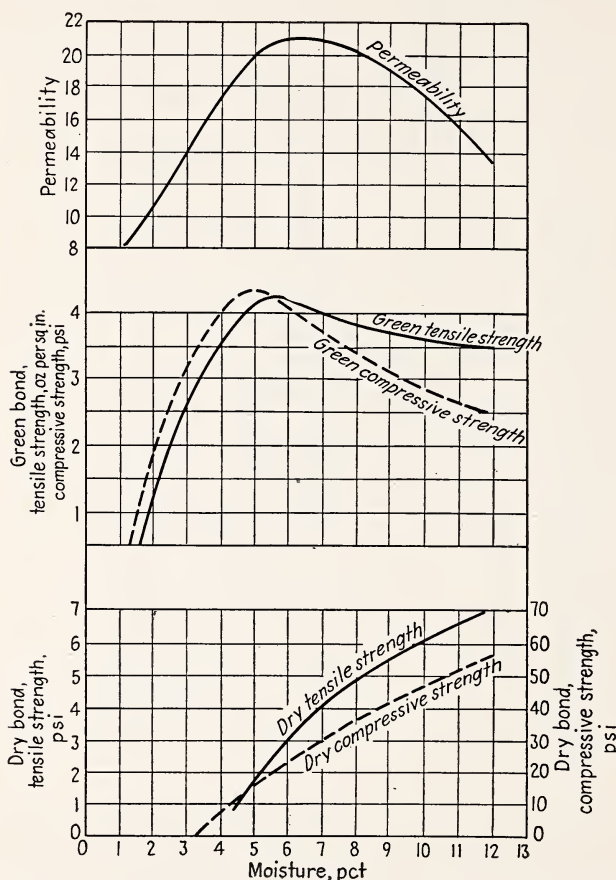


FIG 1—PERMEABILITY AND BONDING STRENGTH OF A MALLEABLE IRON SAND AT DIFFERENT MOISTURE CONTENTS. (After A. A. Grubb.)

the permeability. Variation in moisture content affects the permeability in a manner similar to its effect on strength (Fig 1).

Durability—The durability, or life, of a molding sand is its ability to regain most of its green bonding strength after it has been heated by use and is once again mixed with water. Different sands vary in their durability or life.

Origin and Mode of Occurrence—Most foundry sands are sedimentary deposits of lacustrine or marine origin. They occur in beds

TABLE 2—*Properties of Molding Sands*

Property	Brass Sand			Iron Foundry Sand		
	Light	Medium	Heavy	Large	Medium	Small Casting
Fineness, number.....	220-225	150-200	100-150	25-50	50-100	100-150
Clay, pct.....	6-15	7-10	7-10	10-15	10-15	10-20
Permeability, pct.....	8-12	10-17	17-25	125 up	50-100	20-50
Green, bond tensile, oz.....	4-5	4.3-5.3	4.5-6.0	6-10	4-9	4-9
Compression, psi.....	3-4.5	3-5	3.5-6.0	6-10	4-9	3-8

of varying thickness, and several different grades may occur in the same deposit. These can be separated in excavating the material. Dune sands are sometimes used as a source of supply for core mixtures. Soft white sandstones sometimes are quarried for producing a high-silica sand.

Distribution—While molding sand is obtained locally by many foundries, there are some important centers of production. Prominent among these is the Hudson Valley north and south of Albany, N. Y.¹ Large quantities are also obtained in the Tertiary formations of New Jersey, some being of very coarse texture, spoken of in the trade as gravel. Ohio is also an important producer, pits being worked in the northern part of the state near Conneaut and also in the region around Zanesville. Indiana and Mississippi contribute their share. The Ottawa district of Illinois supplies much silica sand and similar material is obtained in Missouri and Wisconsin. Appreciable amounts of naturally bonded sand are obtained in California, and Nevada supplies a considerable quantity of silica sand. Dune sands are worked at a number of points.

Political and Commercial Control—The factor of political and commercial control enters into the foundry-sand business to but a limited degree, as this country is well supplied. Silica sand from Europe has been shipped by water to Seattle, chiefly because none has been developed near at hand. Sand for bronze casting has been obtained from Europe but the quantity required is limited. On the whole, there is little importation of sand. California sand is shipped to Hawaii for the foundries there, as no local supply has been found.

Production—The output of foundry sand is closely related to the condition of the foundry industry. The production and value for two years are given in Table 3.

Mining—Molding sands are mined by opencut. Steam shovels can be employed where the beds are thick enough, but if they are thin, hand shovels or excavators are commonly employed.

Preparation for Market—High-silica sands such as are employed for cores and synthetic mixtures are usually screened and sometimes also

TABLE 3—*Production of Foundry Sands*^a

Year	Short Tons	Value	Average Value per Ton
1946	6,973,906	\$9,531,263	\$1.37
1947	8,308,434	11,944,228	1.44

^a Mineral Market Report MMS 1655, U. S. Bureau of Mines.

washed. Clay-bonded molding sand may be screened to remove stones, clay lumps, and roots, although this treatment is not always satisfactory if the sand is wet or moist. Either stationary or revolving screens are employed. Some plants put the sand through a milling process: (1) to make the product more uniform; (2) for blending two sands, so as to get a product of the desired quality, or (3) to incorporate clay into one that is deficient in bond.

Tests and Specifications—The tests commonly employed are those adopted as standard by the American Foundrymen's Association.² Permeability is determined on "green" sand at different moisture contents or on the sand dried at 110°C. Strength, which may be compression, tensile, or shear, is carried out on green sand at different moisture contents. The compression and shear tests may also be made on the dried sand. For both permeability and strength, a standard test piece is used. In testing for fineness, the so-called AFA clay is first removed by washing and settling, after which the remaining grain is separated by means of sieves, the numbers used being 6, 12, 20, 30, 50, 70, 100, 140, 200, 270, pan.* From the figures so obtained, the grain-fineness number is calculated.¹⁷ Sintering test is made to determine the temperature at which the grains stick together owing to incipient fusion. The sand may also be tested at elevated temperatures.

There are no standard specifications in the foundry industry but the consumer sometimes purchases sand according to its grade number, which is not the same at all pits; at other times, he may specify that the sand shall show a certain grain-fineness number, strength and permeability, with a tolerance allowance if he chooses.

In foundry control, the sand heaps are tested daily to see that the properties of the material do not vary too much, and this has served to decrease casting losses greatly. No general statement can be made regarding allowable variation, since it depends on a variety of factors.

Marketing and Uses—Sand is sold by the ton. In the foundry industry, it may be used for molds, cores, facing and parting, depending on its properties and fineness.

* This is the series adopted by the American Foundrymen's Association; the numbers refer to the National Bureau of Standards sieves.

GLASS SAND

Sand used in the manufacture of different grades of glass is called glass sand. It may range from high-silica sand, containing but a small percentage of iron oxide, to material with a lower percentage of silica and as much as 1 pct iron oxide. The grains may be round, subangular, or angular. Those from the Ottawa district, Illinois, are often rounded, but most others are angular to subangular. All grains should pass a 20-mesh sieve and there should be little smaller than 100-mesh.

Occurrence and Distribution—Glass sands are found in a number of geologic formations. Those of New Jersey come from the Tertiary, and the Cretaceous of Maryland also affords a supply. Both of these are unconsolidated deposits. The Oriskany sandstone has been worked for glass sand in West Virginia and Pennsylvania and the St. Peter's sandstone (Ordovician) in Illinois and Missouri. Still other supplies come from the Carboniferous in Indiana and Ohio. Glass sand has been produced in a number of states, but West Virginia, Illinois, Pennsylvania, Missouri, and New Jersey are important producers.

TABLE 4—*Production of Glass Sand*^a

Year	Short Tons	Value	Value per Ton
1946	4,848,602	\$9,541,405	\$1.97
1947	5,321,247	11,395,245	2.14

^a Mineral Market Report MMS 1655, U. S. Bureau of Mines.

Mining and Production of Glass Sand—The methods employed for working unconsolidated deposits are much the same as those followed for other grades of sand. Steam-shovel mining is possible but at many plants suction dredges are employed. This is an advantageous method, as the sand has to be washed, and moreover, it undergoes a scrubbing in passing along the pipe line. Stripping should in some instances be carried on in advance of the working, to prevent impure overburden from caving or washing down into the pit where there is danger of this. The consolidated sandstones that are worked are mostly friable and easily crushed. The quarrying methods depend somewhat on whether the beds are steeply dipping or flat. In places, as in eastern Missouri, underground methods are used. In the Ottawa district, Illinois, hydraulic mining is employed. Production and value for 1946 and 1947 are shown in Table 4.

*Preparation of Glass Sand*²¹—The method of preparation used depends on the character of the crude rock or sand, as well as on the grade of sand desired. All sands have to be washed. With unconsolidated sands, the sand and water may be delivered to revolving screens covered with

12 to 18-mesh wire cloth, the oversize being taken away by drags or conveyers. The sand of desired texture and the clay pass through the screens and the excess water carries off the clay.

Where sandstone is used, the rock must first be crushed and ground before it goes to the washers. A washer consists of a cast-iron screw conveyor in a sloping box. As the helix conveys the sand upgrade from one box to another, the overflow water carries off the clay. The washed, dried sand is screened to remove oversize sand and foreign material. Vibrating screens are commonly employed.

In New Jersey, according to Weigel,²¹ the sand is delivered to the washers through a pipe line from the dredge:

"This pipe discharges either to a smaller distributing tank which takes care of the fluctuations in the flow, or may deliver directly to the first screens—revolving screens covered with from 12 to 18-mesh wire cloth. Drags or conveyors take away the oversize. Excess water that passes with the sand through the screens into the tank overflows and carries much of the clay with it. The washers are in effect drag classi-

TABLE 5—Grading of Glass Sand^a

Passing Sieve	Retained on Sieve	Percent-age	Passing Sieve	Retained on Sieve	Percent-age
No. 20.....		100	No. 60.....	No. 100	10-20
No. 20.....	No. 40	40-60	No. 100.....		0-5
No. 40.....	No. 60	30-40			

CUMULATIVE SCREEN ANALYSES OF GLASS SANDS

Mesh Retained on	Sand ^b										
	1	2	3	4	5	6	7	8	9	10	11
14	0	0	0			0	0				
20	0.4	0.6	1.1	0	0	0.1	0.5			0	0
28	1.5	2.9	6.3	0.1	0.6	3.3	3.8	0	0.7	0.1	3.4
35	4.2	13.0	23.0	19.5	17.0	20.3	17.5	1.1	11.6	2.9	30.5
48	12.3	36.8	52.9	60.0	49.7	62.9	56.9	33.6	42.1	23.1	65.0
65	36.7	72.9	84.5	85.7	73.4	90.3	90.9	78.1	74.3	51.3	82.1
100	81.4	95.7	98.6	98.0	87.0	97.5	98.5	94.6	94.6	77.1	92.9
150	97.5	99.2	99.8	99.8	93.6			98.6	99.3	90.6	98.2

^a Recommended by American Ceramic Society and the National Bureau of Standards.

- ^b 1. Williamstown Junction, N. J.
 2. South Vineland, N. J.
 3. Washed and tumbled. Locality not given.
 4. Ottawa, Ill.
 5. Dike, Nev.
 6. Mapleton, Pa.
 7. Mapleton, Pa.
 8. Berkeley Springs, Va.
 9. Wedron, Ill.
 10. Crystal City, Mo.
 11. Ottawa, Ill.

TABLE 6—*Specifications for Chemical Composition of Glass Sands*^a
PERCENTAGE COMPOSITION BASED ON IGNITED SAMPLES

Qualities	SiO ₂ Mini- mum	Al ₂ O ₃ Maxi- mum	Fe ₂ O ₃ Maxi- mum	CaO + MgO Maximum
First quality, optical glass.....	99.8	0.1	0.02	0.1
Second quality, flint-glass containers and tableware.....	98.5	0.5	0.035	0.2
Third quality, flint glass.....	95.0	4.0	0.035	0.5
Fourth quality, sheet glass, rolled and polished plate.....	98.5	0.5	0.06	0.5
Fifth quality, sheet glass, rolled and polished plate.....	95.0	4.0	0.06	0.5
Sixth quality, green glass containers and window glass.....	98.0	0.5	0.3	0.5
Seventh quality, green glass.....	95.0	4.0	0.3	0.5
Eighth quality, amber glass containers.....	98.0	0.5	1.0	0.5
Ninth quality, amber.....	95.0	4.0	1.0	0.5

^a Recommended by American Ceramic Society and National Bureau of Standards.

TABLE 7—*Chemical Analyses of Glass Sands*^a

Source	Composition, Pct					
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Ignition
Crystal City, Missouri:						
Crude.....	99.405	0.210	0.075	0.072	0.068	0.170
Washed.....	99.78					
Mapleton, Pennsylvania.....	99.82	0.12	0.017	tr	tr	
Hancock, West Virginia.....	99.81	0.17	0.014	0.00	0.00	
Ottawa, Illinois.....	99.607	0.160	0.021	0.050	0.03	0.08
W. Vienna, New York.....	98.6	0.17	0.23		tr	

^a From Weigel.²¹

fiers, with their low ends in the tank below the screen. They usually consist of two flights of chain, each fitted with two parallel lines of steel plate scrapers 3 in. wide and 18 in. long. The sloping floor of the drag box, or angle of the chains, is about 30° from the horizontal."

Specifications—Glass sand should all pass a No. 20 sieve but there is a difference of opinion as to the allowable amount smaller than 100-mesh. In any event, the latter is probably small, because most of it is removed by washing. One objection to fines is that they are likely to carry an excess of impurities.

The American Ceramic Society and the National Bureau of Standards recommend the grading of glass sand shown in Table 5, but this is not strictly adhered to by manufacturers.

There are no generally accepted standards for the chemical composition of glass sand, although this property undoubtedly is important.

Individual purchasers may have definite specifications. A minimum of iron oxide is desirable, because of its coloring effect on the glass. Table 6 gives the specified compositions for several types of glass sand. Chemical analyses of various glass sands are given in Table 7.

FILTER SAND

Sand is used by many municipalities to remove sediment and suspended matter, also bacteria, from water.

Properties—The essentials of a filter sand are that it shall be of fairly uniform texture, and that the grain size shall be within certain limits. The grains should be of such a character that they will not be disintegrated by the water. Sands high in silica are regarded as the best. Not more than 2 pct should be soluble in hydrochloric acid. The shape of grain varies from rounded to angular; and, as far as known, these shapes are equally efficient. Flat or elongated grains are undesirable.

Grading—Two terms used to control the average size and uniformity of filter sands are the “effective size” and “uniformity coefficient.”

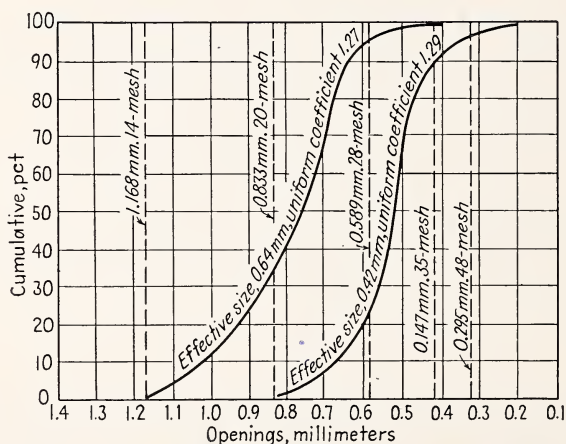


FIG 2—CURVES OF SCREEN ANALYSES OF FILTER SANDS. (After Weigel.)

The effective size of the sand is that size than which 10 pct by weight of the sand is finer and 90 pct is coarser. It is expressed in millimeters, and is determined from a sieve analysis. The uniformity coefficient is the ratio to the effective size of the size than which 60 pct of the sand is finer. If the grains are of uniform size, the uniformity coefficient will be 1. Fig 2 gives the cumulative screen analysis of two sands as well as their effective size and uniformity coefficient.

It is stated that sands with effective sizes of 0.20 to 0.70 mm are used for filtration but those most commonly specified have effective sizes

from 0.35 to 0.65 mm. The uniformity coefficient varies from 1.25 to 1.80, with 1.55 to 1.60 the average.

Distribution—Filter sand has been produced in a number of states from deposits similar in origin to glass sands. Indeed, the two may be obtained from the same formation. New Jersey is an important producer, but much is also obtained from Illinois and Minnesota. A suitable sand can be produced from any good sand bed if it can be properly washed and contains grains of the right size and suitable durability.

Marketing and Production—Owing to the careful preparation required for filter sand, it commands a better market price than ordinary sands. Table 8 gives production and value for 1946 and 1947.

TABLE 8—*Production of Filter Sand*^a

Year	Short Tons	Value	Value per Ton
1946	157,511	\$284,991	\$1.81
1947	211,646	366,905	1.73

^a Mineral Market Report MMS 1655, U. S. Bureau of Mines.

ABRASIVE SAND

Abrasive sand includes all natural sands used for abrasive and grinding purposes. They should be composed of hard grains, and, generally speaking, have a high percentage of silica. They may be used for sawing stone, grinding glass, sandblasting and sandpaper. Those used for different purposes vary somewhat in their character. Artificial sands made by crushing garnet and emery are treated under abrasives.

Production and value of grinding and polishing sand for two years are listed in Table 9.

TABLE 9—*Production of Grinding and Polishing Sand*^a

Year	Short Tons	Value	Value per Ton
1946	906,889	\$1,379,954	\$1.52
1947	1,099,253	1,801,989	1.64

^a Mineral Market Report MMS 1655, U. S. Bureau of Mines. Includes blast sand as follows: 1946—292,899 tons valued at \$739,819; 1947—308,128 tons, at \$958,023.

Stone-sawing Sand—Sand for sawing stone is commonly composed of tough grains and uniformity of size is desirable, fine material being objectionable. However, unsorted sand is often employed Weigel²¹ states that one large marble company uses a clean, washed river sand with 3.7 pct retained on 10-mesh, 12.6 pct on 20-mesh, 83.8 pct on 48-mesh and 98.6 on 100-mesh. The sand after use can be washed to

remove the fines. There are no uniform requirements regarding shape of grain. The sand should be siliceous.

Glass-grinding Sand—Sand is used for rough grinding of crude-rolled plate glass. The requirements are not strict but very fine grains and clay are objectionable. One company employs sand that will all pass 20-mesh and 90 pct of which is retained on the 150-mesh.

Banding Sand—Banding sand, which is used for second or semi-final grinding of plate glass, is considerably finer than that employed for the first grinding. It is less used than formerly, as artificial abrasives have replaced it to a large extent.

Sandblast Sand—Sandblast sand, which by means of an air blast is blown against the surface to be abraded, is used in the foundry for cleaning castings, for removing paint, rust, or stain from old surfaces, for carving designs on stone, and other purposes. The material used for sandblasting is commonly obtained from sedimentary beds of varied origin, but volcanic sand has sometimes been employed.

Blast sands may be separated into different grades, from fine to coarse, No. 1 to No. 4. Table 10 shows their differences. The grade num-

TABLE 10—*Different Grades of Sandblast Sand*^a

Retained on Mesh	Percentages			
	Sand 1	Sand 2	Sand 3	Sand 4
4				2.70
6			0.00	76.60
8			1.55	99.80
10		0.00	53.15	100.00
14	0.40	32.20	84.25	
20	35.70	78.35	99.70	
28	97.20	92.05	100.00	
35	99.90	98.20		
48	100.00	99.70		
65				
100				

^a All from Cape May, N. J.²¹

bers are not to be regarded as accepted standards. A general range of size is: No. 1, through 20-mesh, retained on 48-mesh; No. 2, through 10-mesh, retained on 28-mesh; No. 3, through 6-mesh, retained on 14-mesh; No. 4, through 4-mesh, retained on 8-mesh.

There is no standard requirement regarding the shape of grains of blast sands. Some advocate sharp grains because they are supposed to cut faster, but others believe that rounded grains last longer. Cole⁸ found that rounded grains used on steel plates did not grind as smooth as angular ones when the nozzle was held at an angle to the plate.

ENGINE SAND

Engine sand is used to prevent the driving wheels of engines or the wheels of streetcars from slipping. The requirements are a minimum of fine particles. Either round or angular grains are satisfactory. Different railroads have different specifications, but one specified by the Pennsylvania Railroad system calls for clean silica sand between 20 and

TABLE 11—*Production of Engine Sand^a*

Year	Short Tons	Value	Value per Ton
1946	2,797,132	\$1,924,779	\$0.69
1947	2,683,333	2,092,656	0.78

^a Mineral Market Report MMS 1655, U. S. Bureau of Mines.

80-mesh.²¹ A noncaking quality is important to ensure free running of the sand. Low clay content is desirable to prevent caking. With the decrease in the use of trolley lines, it is probable that the use of traction sand is decreasing. Production and value of engine sand are listed in Table 11 for the years 1946 and 1947.

SAND FOR SHEET ASPHALT

Sand is used in construction of the surface course of asphalt pavements and bituminous-concrete pavements in which sand predominates. The specifications (ASTM) call for grains that are clean, tough, rough surfaced, angular, and free from clay. An asphalt mixture shows an average composition of: sand, 75 pct; filler, 15 pct; asphalt 10 pct. The amount of filler required will be affected by the size of the sand grains. The requirements for grading are given in Table 12.

TABLE 12—*Grading of Sand for Sheet Asphalt*

Passing Sieve	Retained on Sieve	Percentage
No. 200 (74-micron).....		0-5
No. 100 (149-micron).....	No. 200	6-25
No. 80 (177-micron).....	No. 100	6-25
No. 50 (297-micron).....	No. 80	5-40
No. 40 (420-micron).....	No. 50	5-30
No. 30 (590-micron).....	No. 40	8-25
No. 20 (840-micron).....	No. 30	5-15
No. 10 (2000-micron).....	No. 20	5-15
No. 10 (2000-micron).....		95-100
No. 4 (4760-micron).....		100

FIRE OR FURNACE SAND²¹

Silica or sand is used to line furnace bottoms and walls, particularly in open-hearth steel furnaces. It should be high in silica with a small amount of bonding material. Sand with as little as 80 pct silica is sometimes used. If the sand lacks bond, plastic fire clay may be added. A scattering of the different grain sizes is desired, so that the finer ones

TABLE 13—*Production of Furnace Sand*^a

Year	Short Tons	Value	Value per Ton
1946	248,866	\$333,643	\$1.34
1947	373,917	426,956	1.14

^a Mineral Market Report MMS 1655, U. S. Bureau of Mines.

fill the voids between the coarser. They also promote sintering of the bond. Furnace sands in general are similar to fine steel-molding sand. The localities that supply furnace sands are much the same as those from which steel sands are obtained. Pennsylvania, Ohio, New Jersey, and Illinois, therefore, are large producers.

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CHAPTER 46

STRONTIUM MINERALS

By CHARLES L. HARNESS*

STRONTIUM is an essential constituent of celestite (strontium sulphate), of the rarer strontianite (strontium carbonate), and of a few very rare minerals. Celestite is the chief ore but strontianite is more valued except for making the purest strontium salts, because of its ease of processing. The public knows strontium mainly as the source of the red flame in fireworks but it has many other uses.

PROPERTIES

The celestite of commerce is a massive mineral of varying texture: coarsely crystalline, fibrous, bladed, very fine grained or earthy. The color varies greatly with the nature of the impurities but the purer specimens are light blue (Latin, *caelum*, sky) or white. The strontianite of commerce is a massive mineral, more or less coarsely crystalline. The color varies with the impurities. Distinctive characteristics are effervescence with acids, density (3.68 to 3.71), and crimson strontium flame. A typical British celestite before World War II analyzed: SrSO_4 , 96.55 pct; SrCO_3 , 0.17; BaSO_4 , 0.25; CaSO_4 , 0.54; MgCO_3 , 0.15; R_2O_3 , 0.90; SiO_2 , 1.38.¹⁰ A German strontianite analyzed: SrCO_3 , 90.9 pct; CaCO_3 , 7.5; BaCO_3 , 0.1; Fe_2O_3 , 0.05; Al_2O_3 , 0.1; SiO_2 , 0.04; S, 0.1; P, 0.005.¹⁰

ORIGIN AND MODE OF OCCURRENCE

According to Clarke,⁹ strontia forms about 0.02 pct of the crust of the earth and is present in most igneous rocks, but in smaller quantities than barium. Under certain conditions, large masses of celestite are deposited from sea water with anhydrite. The presence of large amounts of celestite in some saline deposits and its absence in others suggests that the deposition of celestite depends on whether certain as yet undetermined concentrations of sulphate and chloride ions are reached in the brines. The most extensive of these sedimentary deposits are those of the Keuper (Triassic) in England, of the Zechstein (Permian) in Germany, and of various Cretaceous formations in Texas, Arkansas, and Utah.

Of the deposits of southeastern California and western Arizona,

* American Cyanamid Co., Stamford, Connecticut.

those at Argos, California; Aguila, Arizona, and Gila Bend, Arizona consist of large amounts of fairly pure (but not necessarily commercial) celestite interbedded with and grading into tuffs. The strontium probably was derived from solfataras. Deposits in the Avawatz Mountains associated with gypsum and manganese may have been formed by the precipitation of solfataric emanations in saline lake waters.

Strontianite is widely distributed but generally in small amounts as the weathering product of celestite.

DISTRIBUTION OF DEPOSITS

United States

Veinlets and masses representing concentration by circulating waters are common in some limestones of the states east of the Mississippi River and in southwestern Michigan and northeastern Ohio, where such masses are abundant enough to be separated by hand sorting in some quarries. Deposits of probable sedimentary origin have been noticed in Burnet, Lampasas, and Travis Counties, Texas, where the Glen Rose (Lower Cretaceous) limestone locally contains from 1 to 10 pct of celestite as nodules and lenticular masses. Similar deposits are found in the De Queen limestone member of the Trinity (Lower Cretaceous) near Martha, Howard County, Arkansas. Lumps and nodules of celestite in clay are found in Brown and Nolan Counties, Texas.²⁰ In the Nolan district, which is representative also of that found in Brown County, the mineral is found in the Double Mountain group of upper Permian age, and the strata comprising the celestite zone consist of soft sands and sandstone, shales, and thin beds of dolomite and dolomite limestone. The celestite appears most commonly in the form of white, somewhat massive crystalline aggregates. An appreciable proportion is in granular form, occurring both as beds and seams.

A deposit worked during World War I occurs one mile southwest of La Conner, Skagit County, Washington.¹⁴ The celestite forms pod-shaped and lens-shaped bodies as much as 30 in. thick in a brecciated zone about 3 ft wide in partly serpentinized dunite. Calcite, dolomite, and limonite are also present, and the celestite is in part altered to strontianite. A similar deposit in the same area was worked in World War II.

A large deposit of celestite lies on the south slope of the Cady Mountains near Argus station, San Bernardino County, California.¹⁵ The celestite is interbedded with shaly and clayey tuff in a zone about 300 ft thick, which crops out for a distance of 4000 ft. The beds are as much as $5\frac{1}{2}$ ft thick and are formed of massive, finely crystalline celestite, locally with small amounts of silica. One of the analyses shows up to 92.6 pct SrSO_4 , and the deposit has been worked commercially.² Celes-

tite deposits associated with gypsum and manganese occur in the Avawatz Mountains, San Bernardino County, California.¹⁵ At one place nearly vertical beds of celestite as much as $3\frac{1}{2}$ ft thick are interbedded with gypsum over a distance of about 1000 ft. A bed of celestite about 10 ft thick overlies a gypsum bed about 150 ft thick in the Fish Mountains, Imperial County, California.

Strontianite occurs in clayey and shaly tuffs in the low hills about 10 miles northeast of Barstow, San Bernardino County, California.¹⁵ The strontianite forms concretionary masses in the tuffs and most of it is not of commercial value. A deposit of celestite 40 miles northwest of Westmoreland, in the Superstition Mountains, Imperial County, California, occurs as a flat bed overlying gypsum.¹ This bed supplied the bulk of domestic chemical-grade celestite consumed in the United States during the late war.

A large deposit of celestite occurs in the Vulture Mountains, Maricopa County, Arizona,¹⁵ 15 miles southeast of Aguila. The celestite forms beds as much as $3\frac{1}{2}$ ft thick in a series of shaly tuffs. It is more or less silicified. Some material was shipped from this deposit during World War II.⁴ Celestite forms steeply dipping beds in a series of sandy tuffs about 15 miles south of Gila Bend and 3 miles east of Black Rock siding. The zone is reported to extend for a mile, and for a distance of 750 ft the main bed is 2 to 3 ft thick.

Celestite aggregates, up to $1\frac{1}{3}$ ft in diameter, occur in Glen Deam limestone in Fentress County, Tennessee, near Jamestown.¹³ The aggregates comprise a little less than 6 pct of the total rock and give the appearance of snowballs spattered against the working face. During the war, some of this material was recovered by crushing, jigging, and tabling but, despite the high purity of the concentrate (96 + pct SrSO_4 , Ba absent), the cost proved prohibitive.

Foreign Countries

Canada—Spence¹⁷ has described in some detail deposits of celestite and barytocelestite in Canada. Hydrothermal veins 1 to 3 ft thick, with one or both walls in limestone, are known in Ontario in Fitzroy Township, Carleton County; Loughborough Township, Frontenac County; Landsdowne Township, Leeds County; and Bagot Township, Renfrew County. The Bagot deposit has been worked in an open pit and a small mill erected. Here the celestite contains 14 to 18 pct of barium sulphate and forms a much broken vein 2 to 3 ft thick in dolomite. The vein has been greatly disrupted during crushing of the dolomite. It is worked in an open pit, and about 30 pct of the barytocelestite can be recovered by hand methods. The rest is separated by milling.

Other deposits are known near Birch Island, 80 miles north of Kamloops, British Columbia, and in Cape Breton County, Nova Scotia.

England^{6,16}—Both strontianite and celestite are found at many localities in England and Scotland but commercially important amounts of strontium minerals appear to be limited to the celestite deposits of Gloucestershire and Somerset. The celestite occurs as irregular masses and lenticular bodies associated with similar bodies of gypsum in the Keuper marl (Triassic), and in smaller quantity in the Keuper dolomite conglomerate (Triassic). Celestite also fills clefts in the floor under the Keuper. Some of these fillings are as much as 3 ft wide, 40 ft long, and 20 to 30 ft deep.

The deposits have been worked at various places in Somerset and Gloucestershire since 1874 but in recent years the workings have been confined to a strip about 1800 ft wide running from Yates as far south as Golden Valley, a distance of about 7 miles.

France—The only celestite deposit of commercial importance in France is 6 miles from Nyon, near Condorcet, in the Department of Drome. Output reached 3000 metric tons in the '20s but ordinarily is much lower.

Germany—Celestite deposits of commercial interest as described by Baertling occur at various places in Westphalia in the upper Zechstein (Permian). The best deposit is that near Obergembeck. It lies on a ridge, in two parts. On the north side of the ridge, celestite forms a strip from 33 to 99 ft wide and 1500 ft long, and on the south side another strip of about the same width and 660 ft long, both in dolomite. On the crest of the ridge, in the underlying Kulm (lower Carboniferous), there are numerous scattered masses of celestite as much as a cubic yard in size. The celestite contains as much as 94 pct SrSO_4 . The deposit originally was estimated to contain 50,000 metric tons but has been depleted by working. Near Giershagen, celestite forms small masses 1 to $2\frac{1}{2}$ ft thick and a larger body 3 to $5\frac{1}{2}$ ft thick underlying an area about 50 to 75 ft wide and 1650 ft long. The material is thinly banded, red and yellow, fine grained and cavernous, with some druses. The quantity present was estimated to be about 20,000 metric tons. The SrSO_4 content in this deposit is more than 90 pct. A body of bluish white and red celestite about 40 in. thick was discovered in the upper Zechstein (Permian), near Helmscheid, in 1902. It contains about 25 pct silica and therefore has not been utilized.

The chief sources of German strontium in the past were the valuable strontianite deposits of the region about Muenster, in Westphalia, which are described by Becker.⁷ Numerous irregular veins cut the Upper Cretaceous marls of the region. Strontianite is irregularly distributed in these veins as lenticular masses as much as $7\frac{1}{2}$ ft thick, but usually not more than 10 in. Fillings show a bilateral structure, with calcite next the walls and strontianite, commonly banded, in the center. Pyrite occurs in small crystals on both calcite and strontianite and forms

masses in the marl walls. It is commonly believed that the deposits do not persist to depths of more than about 65 ft but Becker cites one set of workings that reached 312 ft and believes that there is a larger tonnage left in the district at lower levels than have yet been worked.

Russia—Baertling⁵ mentions deposits of celestite similar to those of Sicily, in the Pinega River region of Archangel Province, USSR. The celestite is said to form large masses of blue color and excellent quality.

Sicily—Large amounts of celestite are associated with the sulphur deposits of Sicily. The celestite is crystalline and forms large irregular masses as well as crystals but has not been described in detail. Large deposits are found near Girgenti and Caltanissetta but regular production has not yet been established, though at times it has been large enough to set the price for English celestite.

India—It is stated that large deposits occur in the Trichinopoly district, Madras.¹⁹

Mexico and Spain—Two new sources of celestite were developed during the war, Mexico and Spain. In Mexico, deposits were first worked near Matehuala, S.L.P., in 1941, and later near Monterrey. During the war, this material was shipped overland by rail through Laredo and El Paso. However, water shipment via Tampico is the logical route in peacetime. In Spain, celestite was mined near La Malaha and Alhendrin, Province of Granada, and purchased by a United States Government stock-piling agency for overland shipment to Motril, on the Mediterranean, and thence to American coastal consuming points.

PRODUCTION, IMPORTS, AND PRICE HISTORY

In the United States, the main output of celestite has come from Brown and Nolan Counties, Texas, mostly for use in oil-well drilling muds. The greatest output for chemical uses has come from a mine near Westmoreland, Imperial County, California. Arizona, Washington, and Tennessee have also accounted for relatively small quantities.

TABLE 1—*Domestic Production of Celestite, 1916–1918 and 1940–1947*^a

No data available for 1919–1939. No production known except in Texas in 1938 and 1939 for well drilling.

Year	Short Tons	Year	Short Tons	Year	Short Tons
1916	250	1940	350	1944	3,005
1917	4,035	1941	4,724	1945	2,784
1918	400	1942	4,041	1946	243
		1943	7,566	1947	Negligible

^aData (supplied by U. S. Bureau of Mines) include both chemical and nonchemical grades of celestite as well as small quantities of strontianite and mixed celestite-strontianite.

England and Germany supplied nearly all the strontium minerals imported into the United States until the late war, at which time Mexico and Spain became the major sources. Imports are shown in Table 2.

TABLE 2—Imports of Celestite and Strontianite into the United States by Countries of Origin,
1939-1947^a
SHORT TONS

Year	Germany	Mexico	Spain	Tunisia	United Kingdom	Total
1939	^b			11	2,861	2,872
1940				22	2,729	2,751
1941		987			3,306	4,293
1942		6,201	1,475		2,682	10,358
1943		11,060	4,454		1,367	16,881
1944		3,170	2,622		1	5,793
1945		3,016	675			3,691
1946		1,977			2,530	4,507
1947		3,937	5,836		4,344	14,117

^a Data from U. S. Department of Commerce.

^b Less than one ton.

The first commercial production of strontium was in Germany. According to Becker,⁷ production from the Westphalian strontianite deposits began in 1840 and rose from 30 to 200 metric tons a year by 1875. With the introduction of processes using strontium hydroxide for desaccharizing beet-sugar molasses, the production was stimulated and rose to a maximum of 7883 metric tons in 1884. The demand for strontium salts led to production from the English deposits in 1875, although these had been known since 1799. By 1884, English celestite had obtained a dominant position and from that time to the first World War the total production of 5,000 to 20,000 tons a year was exported to Germany for processing. Most of it was used in the German beet-sugar industry and the rest was exported as finished salts, mainly the nitrate. During this period the production of strontianite declined steadily and after the war it averaged only about 100 tons a year until 1930, when it began to rise. Since World War I, there has been some production of celestite in Germany but data are not available.

The price of English celestite at the quarry¹⁶ was £2 a long ton in 1884. In 1885, it decreased to 5 shillings a ton but in the period 1893 to 1903 it rose to £1. From 1903 to 1907, it decreased to 15 shillings a ton. In 1915, the price at the Bristol dock was about 14 shillings 2 pence (\$3.45) a long ton, and in 1933-1934 about \$7 a short ton, or about \$10 a short ton delivered at Atlantic Coast ports. During World War II, the comparable price was \$30 to \$35. In 1946 imported crude celestite was worth about \$28 to \$30 a short ton laid down at Philadelphia.

The price of German strontianite⁷ was about 400 marks per ton in 1876 but ranged around 150 to 200 marks during the period just preceding World War II. The price is limited by the cost of manufacture of competitive strontium carbonate from celestite. The cost of strontia-

nite is commonly 5 to 10 pct less than the cost of the synthetic carbonate.

Up to the time of World War I, the United States imported sufficient strontium salts from Germany to meet the needs of the pyrotechnic, chemical, and drug industries. When this trade was shut off, celestite was imported from England until the embargo of 1917, which greatly stimulated domestic production. With the entry of the United States into the war in 1917, the embargo was lifted, but, even so, domestic production of celestite for 1917 was over 4000 tons. In the interwar period, the domestic demand for strontium was met by imports of English celestite and finished German salts.

MINING AND PREPARATION FOR MARKET

The production of strontium minerals always has been carried on in a small way and by simple methods. The English deposits are prospected by sounding the soil with long rods. The hard masses thus located are mined in pits, and may be found to be either celestite or gypsum. Most of the workings are less than 20 ft deep but where masses are found in clefts in the underlying formations, workings may be deeper. The celestite lumps are washed and trimmed by hand.

In Brown and Nolan Counties, Texas, celestite is broken from undulating beds 2 to 20 in. thick by means of horse-drawn plows, sorted roughly, and hand-loaded. In the Fentress County, Tennessee, area, during the brief period in which celestite was produced there, it was crushed and tabled to separate it from its limestone matrix.

During the late war, the celestite supply was increased by beneficiating impure material available in Brown and Nolan Counties, Texas, analyzing 70 to 85 pct SrSO_4 . The Bureau of Mines developed a flotation process that recovered celestite meeting wartime specifications,¹¹ and a chemical manufacturer in Philadelphia also beneficiated Texas celestite on a commercial basis by grinding and tabling.

Specifications

Prior to World War II, celestite analyzing less than 95 pct SrSO_4 was purchased ordinarily only on a penalty basis. However, owing to shortages of this mineral during the war, specifications were relaxed; most buyers required only 90 pct SrSO_4 minimum and permitted up to 4 pct Ca (as sulphate) and 4 pct Ba (as sulphate). Since the war's end, specifications have again become more stringent and a minimum of 95 pct SrSO_4 is again being asked, with low calcium, barium and iron. Lump material is preferred but fines are accepted occasionally.

MARKETING AND USES

Marketing—Domestic chemical-grade celestite is loaded usually in gondola freight cars for shipment to the handful of chemical plants

that process this mineral. Subchemical-grade Texas celestite is ground and shipped to oil-well drillers as a drilling-mud weighting agent. During the war some of the best Texas material, although still subgrade by even wartime standards, was shipped east for mixture with richer imported chemical-grade material, and some has also been shipped to local manufacturers of caustic soda for alkali purification.

In England, gravity concentrating equipment has been installed recently but in the past the Gloucestershire celestite was hand-cobbed at the pits, carted to Yate and other stations on the Midland Railway, and loaded on ships at Bristol for export to Philadelphia and other Atlantic ports. Generally it takes a ballast rate. Although minor quantities of strontianite have been exported from the Westphal mines in Germany, by far the major portion of German trade in this field has been in strontium salts (especially the nitrate), which are easily made as by-products of the Scheibler desaccharization process.

Uses—Celestite has been used as a weighing agent to control pressures in drilling oil wells by the rotary method. For this use it competed with barite from 1938 until 1943, when the patent on the use of barite in drilling wells expired, thereafter relieving well-drillers of paying a royalty. Thus the use of the heavier and more suitable barite suddenly became as cheap as the use of celestite. Since 1943, this outlet for celestite has been negligible. Ground celestite is used to remove traces of iron from caustic soda solutions.⁸ This is a small but growing commercial use. Raw strontianite has been used in desulphurizing steel.¹⁰ All other uses of celestite and strontianite involve conversion to other strontium salts, the nitrate being of main importance. Celestite is commonly digested in a soda-ash solution, yielding the less soluble strontium carbonate, and this is treated with the appropriate acid to make the desired salt.³

The main use of strontium salts is in red-flame pyrotechnic compositions. The main war use was in tracer bullets and signal flares. In peacetime, the chief use is in truck signal flares, to warn motorists of breakdowns, and on railroads. The flare generally has a fuse that can be ignited by striking it like a match, and a spike in the bottom of the flare permits thrusting it upright into the ground.

Strontium carbonate is finding a gradually expanding use as a lead replacement in certain enamels and frits, and strontium greases, which are water and hydrocarbon resistant, have recently received attention.²¹

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SULPHUR AND PYRITES

BY W. T. LUNDY*

THE forms in which sulphur is commonly found—native sulphur, sulphides of many metals and sulphates—are widely distributed throughout the world. The two first mentioned are the principal sources of sulphur. Substantial amounts of sulphur in some form are recovered from gases from industrial plants and from gases from smelters treating other minerals. In recent years, plants have been installed in the United States to recover sulphur in elemental form from sour gases.⁸² The amount of sulphur so produced is small at the present time but undoubtedly will increase in the future. The recovery of sulphur from gases is not covered in this chapter, which is confined to: (1) native sulphur deposits of Texas and Louisiana; (2) those of Italy; (3) other scattered deposits of native sulphur; and (4) pyrites deposits found in many countries of the world.³⁰

Sulphur, a nonmetallic element, occurs normally in well developed bipyramidal or tabular crystals of the orthorhombic system, as well as in stalactitic and earthy masses. The mineral has a distinctive yellow color, which may be dark and discolored by impurities; the streak is white; the luster is resinous; and the fracture is conchoidal to uneven. Sulphur is translucent to opaque; has a hardness of 1.5 to 2.5, a specific gravity of 2.05, and an atomic weight of 32.06.¹⁶ The molecular weight of the solid is expressed by the symbol S_8 and that of the liquid and vapor ranges from S_2 to S_8 , depending on the temperature. Sulphur melts at a temperature between 234° and 248°F, depending on its crystalline state, to a liquid of dark amber color, the boiling point of which is 832°F. The viscosity near the melting point is about that of water and increases to 50,000 times that of water at a temperature of 380°F, subsequently falling rapidly to a low figure at the boiling point. Crystallization changes slowly from rhombic to monoclinic above 205°F and in cooling the transformation is reversed. The mineral is a very poor conductor of heat and electricity; it is insoluble in water and nearly all acids and is soluble in cold carbon bisulphide and carbon tetrachloride. It ignites in air at a temperature of 478°F, burning with a distinctive blue flame with evolution of sulphur dioxide.⁴⁷

* Vice President and Director, Freeport Sulphur Co., New York, N. Y.

SALT-DOME SULPHUR DEPOSITS

The sulphur deposits within the area bordering the Gulf of Mexico in Texas and Louisiana are of primary economic importance because of their known and potential reserves, their productive capacity, the ability to market this basic commodity at a reasonable price, and the unequaled purity of the product as mined. These are the commonly called salt-dome type²⁶ of deposits. The structures with which sulphur is associated may be described as submerged islands of rock lying at irregular intervals in a sea of unconsolidated sediments of great areal extent and unknown depth.*

Sediments—The territory in which these domes are found is uniformly low-lying and flat, with little topographical relief other than occasional mounds, which evidently are the result of salt-dome intrusion. The areas contiguous to the Gulf of Mexico, and extending irregular distances inland, are composed largely of sea marshes with numerous shallow bays, lagoons, lakes, and bayous. The surface farther inland rises very gently by a series of inconspicuous terraces, probably former shore lines, and finally merges at its interior border into a low, rolling terrain. Drilling has not reached depths much greater than 15,000 ft but it is generally assumed that sedimentary formations are not less than 20,000 ft thick, as illustrated in Fig 1. The formations dip and thicken in a southerly direction toward the Gulf of Mexico and they have a slight pitch in an easterly direction. It is evident that the sediments were deposited when and where the larger streams met encroaching waters of the Gulf of Mexico. Geologists are now able to describe this process in great detail and apparently to reach logical conclusions on the age of formations and methods of deposition as a result of intensive drilling for the past 30 years.^{7, 67, 71}

Salt—The salt, which is the basic formation of all domes of the Gulf Coast, is an essentially dry, compact, and coarsely crystalline halite. Anhydrite is the principal accessory mineral and, occurring as scattered grains and small crystals of sand size, averages from 5 to 10 pct of the salt mass. The top of the salt on some domes is rather flat, while others exhibit a domal or anticlinal shape. Salt domes usually have a circular outline with steeply dipping flanks but some show an elliptical tendency in configuration. In a few instances, salt lies within 100 ft of the surface and in contact with unconsolidated sediments, but usually it is immediately overlain with cap rock. Available evidence indicates that salt has intruded the sediments at great depths from mother beds of unknown geologic age. Weight of the sediments upon the salt evidently is the force that caused the intrusion. A factor that has been suggested

* Publications of the American Association of Petroleum Geologists contain numerous papers on Gulf Coast stratigraphy and salt-dome geology.

as contributing to the present position is subsidence of sedimentary formations resulting from settlement of the basement series.^{6,17,50}

Cap Rock—Cap-rock formations,^{10,24,73} consisting of limestone, gypsum and anhydrite and underlain by salt, differ materially in features such as size, depth, thickness, and configuration, as well as in the relative proportions of principal and accessory constituents.²⁷ Typical cross sections of sulphur-bearing cap rock are illustrated by Fig 2. The mineralogical basis of this series of formations is a hard and dark gray

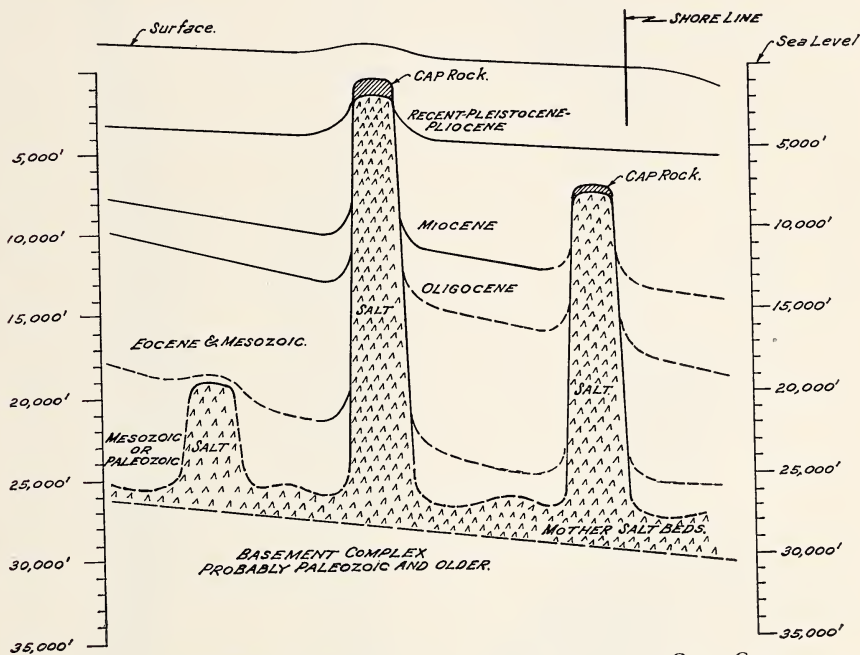
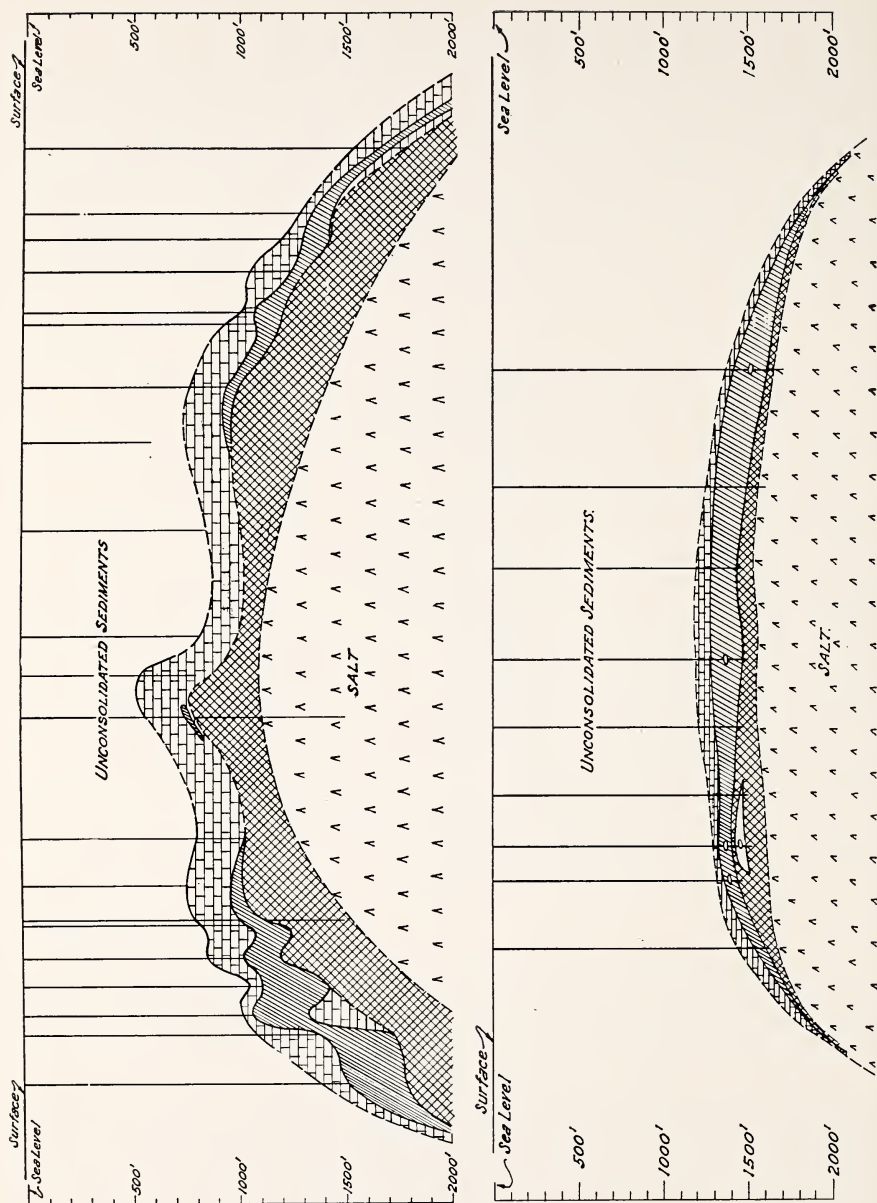


FIG 1—THEORETICAL CROSS SECTION OF PART OF LOUISIANA GULF COAST.

Showing estimated depths to older formations not reached in drilling, "mother salt beds" and basement complex, and the relationship of different types of salt plugs to the sediments. Adapted from Storm⁷¹ and others.

anhydrite superimposed on and lying in contact with salt. Gypsum, when present, may be a dense gray variety or a porous white material containing lenses, nodules, and well developed crystals of selenite. Limestone strata are relatively large in comparison with gypsum and anhydrite. Limestone may be present as a single stratum, as a series of lenticular beds covering only a portion of gypsum and anhydrite, or in disseminated lenses and nodules included in the upper portion of the series. The limestone is typically a fine-grained gray carbonate interspersed with vugs, seams, fissures and cavities, which may be partly or wholly filled with calcite. Siliceous solutions have frequently indurated the limestone in the upper portions, where it is usually barren of



sulphur. Domes exhibit variations in thicknesses of cap rock from less than 50 ft to more than 1000 ft. A universal constituent of cap rock is water highly charged with hydrogen sulphide, polysulphides, sodium chloride, and other salts, and having a temperature of approximately 100°F.

Current publications discuss two principal processes, with minor modifications, explaining the origin of cap rock, and both of these assume

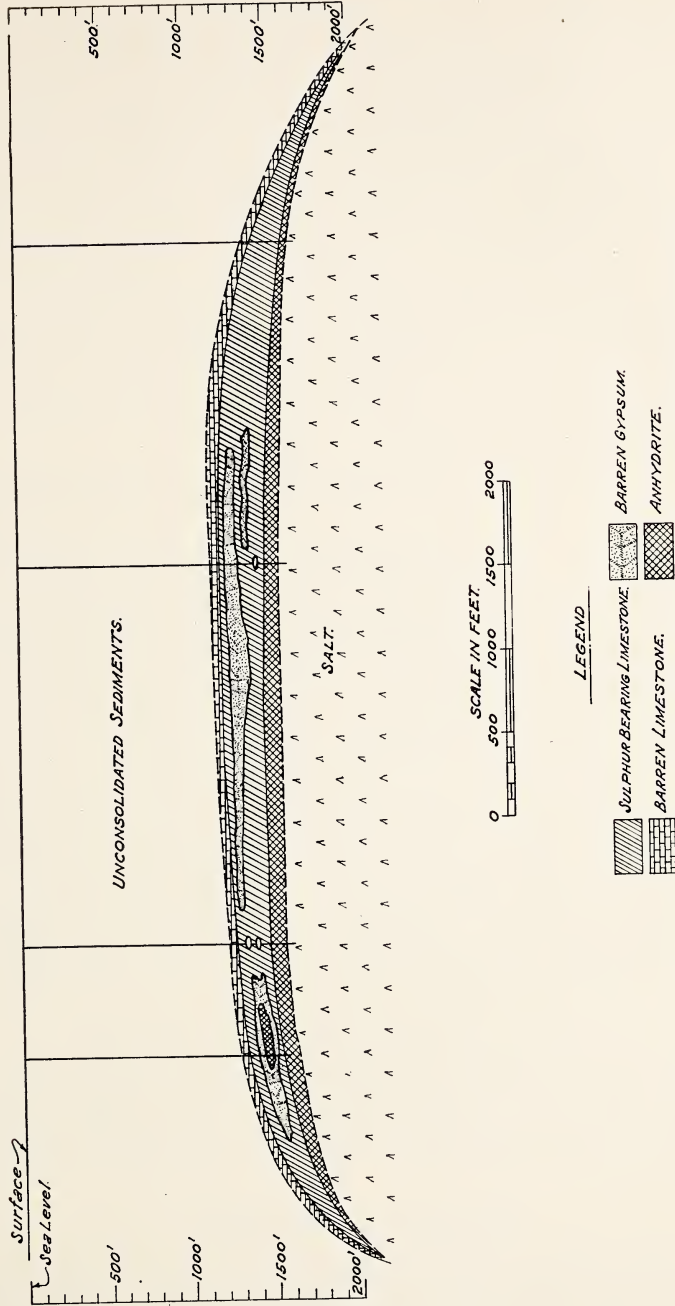


FIG 2—TYPICAL CROSS SECTIONS OF SULPHUR-BEARING CAP ROCK ON SOME SALT DOMES.

the intrusive origin of the salt structure. One theory is that anhydrite was an original formation with and overlying the salt beds before inception of the movement and that it has been lifted to its present position with the salt.^{10,24} The other theory is based on the assumption that circulating waters dissolved vast quantities of salt during its upward movement. Its anhydrite content was thus concentrated as an insoluble residue on top of salt. Anhydrite was subsequently compacted and recrystallized by the same forces causing the salt intrusion, into the hard and dense cap rock that lies as a mantle on nearly all salt domes.^{23,26,73,78} Both theories assume that gypsum was formed by hydration of anhydrite. Structural and petrographic studies indicate that limestone, at least in part, is an alteration product of these formations. The amount of coarsely crystalline calcite present is very suggestive of the important part played by circulating waters.

Sulphur Formations—Sulphur of mineralogic interest is quite persistent in many cap-rock formations but deposits of sufficient size to warrant development have been found on a small percentage only of the known domes. The principal deposits usually are confined to the lower parts of the limestone and in some places substantial amounts extend into the gypsum. Sulphur occurs as well-developed crystal aggregates in the seams and cavities of the porous limestone and also in a semicrystalline or massive state as a filling in the openings of formations. The thickness of the barren cap rock varies from a minimum of 5 or 10 ft to a maximum of 200 ft. The thickness of the sulphur horizon is seldom less than 25 ft and may reach 300 ft as a maximum, the average for bodies of economic size approximating 100 ft. For a few feet, sulphur may be in practically pure state, but the average content of formations for the various deposits ranges from 20 to 40 pct. These deposits differ markedly in reserves, as illustrated by mines that have been depleted. Sulphur, Louisiana, with a cap-rock area of 75 acres, produced 9,412,165 tons; Bryanmound, Texas, with a cap-rock area of 800 acres, produced 5,001,068 tons; Palangana, Texas, with a cap-rock area of 1800 acres, produced 236,662 tons; Gulf, Texas, with a cap-rock area of 300 acres, produced 12,000,000 tons; Jefferson Island, Louisiana, with a cap-rock area of 400 acres, produced 438,811 tons. The average porosity of the sulphur-bearing formations is generally assumed to be between 15 and 25 pct.

Distribution of Salt Domes

The area in which coastal salt domes are found extends from slightly east of the Mississippi River to the vicinity of Corpus Christi, Texas, and inland from the Gulf of Mexico for approximately 75 miles. The presence of 119 domes has been definitely established by drilling within this territory, comprising nearly 45,000 square miles. Many other

deeper structures have been indicated by geophysical surveys. Most of the proven structures have been prospected for sulphur, some more thoroughly than others. Production of importance has been secured from 12 domes, which include Sulphur, Louisiana, by the Union Sulphur Co.;³⁶ Bryanmound,³⁸ Hoskins Mound, Texas,⁴⁴ and Grande Ecaille, Louisiana,⁴¹ by Freeport Sulphur Co.; Gulf,⁸⁵ Newgulf (located on Boling dome⁸⁶), Long Point, and Moss Bluff, Texas, by Texas Gulf Sulphur Co.; Palangana, Boling (on Boling dome), and Orchard, Texas, by Duval Texas Sulphur Co.; and Jefferson Island, Louisiana,⁵¹ Clemens, and Long Point, Texas, by Jefferson Lake Sulphur Co.

There are known salt domes or similar structures in regions other than the Gulf Coast of Texas and Louisiana but none of them has reserves worthy of development. Those best known include interior domes of Texas;⁵⁴ interior domes of Louisiana;⁶⁸ Rumanian salt domes;⁸¹ German salt domes;⁷⁰ salt domes of the Isthmus of Tehuantepec; Persian salt domes;²⁸ the Emba region of USSR;⁶³ and salt structures in Colorado and Utah.²⁹

The discovery of a salt dome in Mississippi in 1937 established the presence of a new salt-dome basin, which was found to extend into Louisiana and Alabama by subsequent drilling. Additional domes were rapidly discovered and by October 1948 there were 42 proven domes. Although 21 of the shallow domes in the Mississippi basin have been prospected for sulphur, no deposits of importance have been developed. As a result of geophysical surveys started in 1944, six salt domes have been proven in the maritime strip that extends seaward from Louisiana and Texas coasts. It is expected that additional domes will be discovered in this area, which is geologically an extension of the coastal salt-dome basin. The potential value of this maritime strip, from the standpoint of sulphur, is questionable, owing to the great hazards and high costs that can be visualized for mining sulphur at exposed locations in the Gulf of Mexico, where the depth of water ranges from 20 to 50 ft.

Exploration and Mining of Salt-dome Deposits

Since 1924, geophysical methods have played an important part in prospecting and locating structures favorable for sulphur deposits.^{64,89} The normal procedure includes seismograph and gravity-meter surveys of large areas. When rock structure is indicated, it is customary to supplement the seismograph or gravity meter with a torsion balance to secure more detailed information on size, depth, and configuration of cap-rock area.⁵ A few wells may then be drilled at scattered locations at distances ranging from 500 to 1000 ft or more. When sulphur is encountered, a systematic drilling and sampling program is carried out.⁴¹ Conventional oil-well rotary equipment is used. The accurate sampling of sulphur formations for estimation of reserves is difficult because of the

loss of returns in porous formations and also because of soft, friable nature of sulphur, which may lead to the impoverishment of samples when coring. Bailers and sand pumps are used to recover cuttings and thus improve coring results. The reverse return with air is another method commonly used. An airlift by this method induces a flow of water and cuttings into the drill stem and to the surface equipment for dividing and settling. This method is considered less expensive and more accurate than coring.⁴⁴

The early history of the Frasch process at Sulphur, Louisiana, was recounted with great interest by Herman Frasch in an address upon receipt of the Perkin medal.²¹ Since then a number of deposits have been found, developed, and a few abandoned because of depletion. Publications for the past 20 years contain comprehensive descriptions of methods and practices.^{51,58,74,86} Typical well equipment and the principles of sulphur mining by the Frasch process are illustrated by Fig 3. The following discussion will be confined to a few specific phases of the subject.

The Frasch process requires water in quantities varying with size of plants from 1,000,000 to 10,000,000 gal per day. The water, being heated from atmospheric temperature to at least 300°F, must be fairly pure originally and must be carefully treated to control corrosion and scale. In comparatively recent years, improvements in water-treating processes and equipment have added materially to the efficiency of power plants.^{3,37} High-pressure boilers, which require water of good quality at all times, contribute to high efficiency and to a favorable heat balance by maximum use of exhaust steam. Sulphur deposits of Texas and Louisiana have been generally fortunate in lying in close proximity to large rivers. The water occasionally becomes high in salt content where mines are situated near the Gulf of Mexico, and large reservoirs are employed to store good water when available. Fuel to heat the water usually constitutes one of the largest items of expense. A reliable supply at reasonable costs is therefore an important factor in production of sulphur by the Frasch process.

In equipping a sulphur property for production, probably the largest single item of cost is the central heating and power plant.⁵² The first requisite for the plant is continuity of operations because interruption of hot water to wells would endanger their loss by freezing of sulphur. The principal function of boilers, the largest part of power-plant equipment, is to convert one fourth of the water to steam. The temperature of all the water is then raised by the steam in mixing-type heaters to that required for mining purposes. The plant also furnishes steam for turbine-driven centrifugal pumps to transport water through thousands of feet of insulated pipe lines to wells and underground formations. It also has equipment for compressing air for raising the liquid sulphur to the sur-

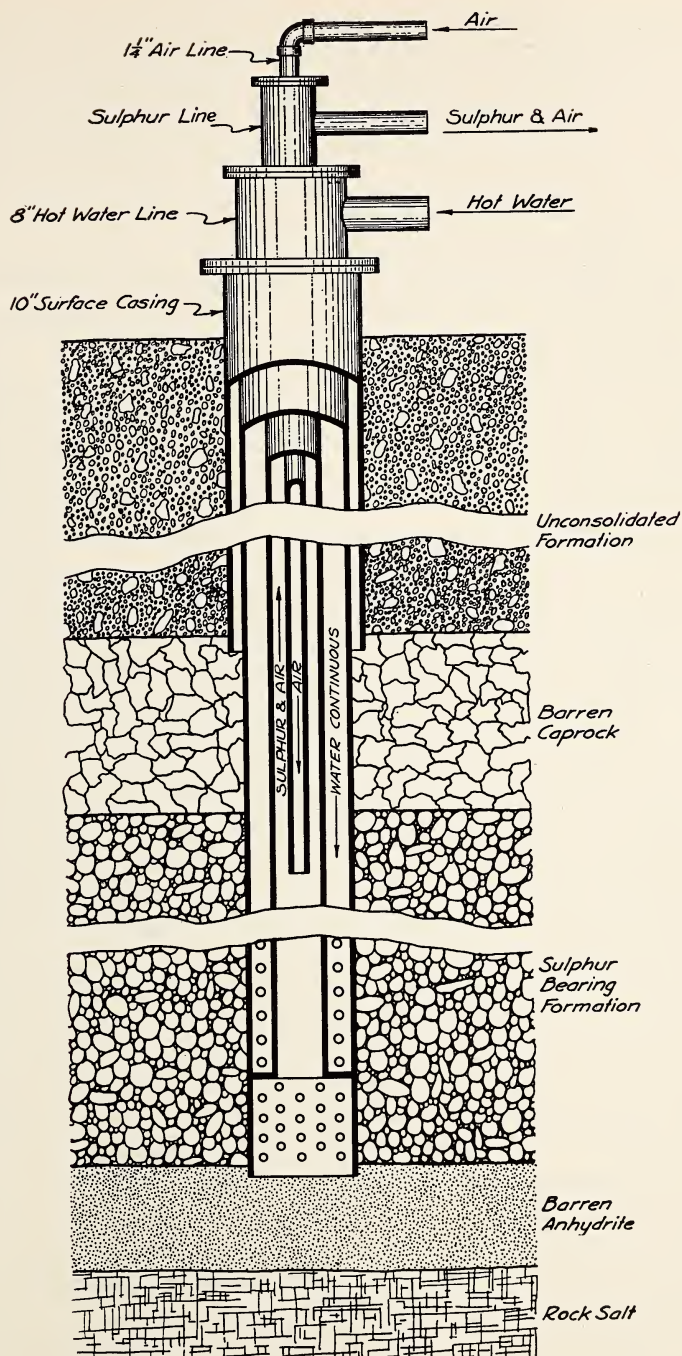


FIG 3—TYPICAL WELL EQUIPMENT FOR SULPHUR MINING.

face, as well as electrical equipment to generate power. Electrically operated equipment is now used for many purposes such as drilling, lighting, pumping water and liquid sulphur, loading and transportation of sulphur, and operation of maintenance facilities including machine, blacksmith, carpenter, and electric shops. Waste formation water, about equivalent in volume to that used for mining purposes, can be treated with plant stack gases or aerated to eliminate the sulphide content before disposal.¹⁴ Modern plants for sulphur mining have attained a comparatively high degree of efficiency. From 75 to 80 pct of total heat in the fuel is put into the water by boiler equipment, and, in addition, a substantial part of the heat in stack gases can be utilized.

The Bryanmound sulphur deposit, except for two short suspension periods, was in operation from 1912 to 1935. At one period in its history, Bryanmound, with an installed plant capacity of 23,000 boiler horsepower, delivered daily about 9,000,000 gal of water for mining purposes with a fuel consumption of approximately 4500 bbl of oil. The cap-rock area comprises approximately 800 acres but the major part of production was secured from 296 acres. During the life of Bryanmound, 1897 wells were drilled. The average production was 2635 tons per well.

The maximum depth from which sulphur can be mined by the Frasch process has not been established. Depth limitations probably will be determined by costs rather than by engineering difficulties. Sulphur has been produced profitably from 2300 ft at Hoskins Mound, Texas. Mining from very shallow depths could involve problems in maintenance of necessarily high temperatures and pressures for water.

Formation conditions that are favorable for the Frasch process include a thick and rich deposit of sulphur; absence of overlying barren cap rock, which retards or prevents subsidence of upper sedimentary formations into cavities; impervious strata above and below the sulphur deposit to prevent escape of hot water; and a uniform porosity to assist in an even distribution of hot water. A substitute method for filling the largest voids and channels in the rock structure has been developed because subsidence does not always take place naturally and quickly. The desired effect is a more uniform porosity to increase the efficiency of hot water. Mud is pumped into wells, at locations remote from mining areas, until the pressure reaches 200 or 300 lb. The amount of mud applied varies greatly, ranging from 25,000 to more than 300,000 cu yd per well. Innovations in methods of applying mud to formations offer interesting avenues for improvements in mining sulphur.

Sulphur produced by the Frasch process is exceptionally free from foreign materials and by analyses shows a very small ash content, usually less than 0.01 pct. An explanation for this fortunate condition is the relatively greater wettability of gangue rock compared with sulphur. Thus the fine gangue rock when wet by hot water is either washed away

from the vicinity of the well or floats on the surface of liquid sulphur and does not contaminate it. Organic impurities, such as petroleum residues, soluble in sulphur, infrequently contaminate and discolor the product. When this occurs quality and color can be improved by distillation or by adsorption.

ITALIAN SULPHUR DEPOSITS

The sulphur deposits of Sicily are among the outstanding mineral deposits of the world, owing to their long history and their known and potential reserves. Unique methods of beneficiation developed under adverse conditions add further interest to the history of these deposits. The Italian sulphur industry⁷⁹ has experienced vicissitudes of many kinds. Development of the Frasch process resulted in a severe reduction in its markets and the value of the product. In addition, the recent war caused complete suspension. The resumption of operations has been slow, difficult and expensive, as illustrated by production. In 1939, the production was 350,208 tons; in 1944, it was an estimated 37,000 tons; and in 1947, it was 169,273 tons.⁴⁹

Formations—An ideal section of formations includes yellow, loosely cemented sandstone, argillaceous marls and blue clay, foraminiferous limestone interbedded with clay, and below this series of sediments the gypsum and sulphur-bearing formations. The entire region was subjected to severe faulting and folding which, together with erosion, complicated the regional geology and resulted in a rolling and semimountainous terrain. The sulphur-bearing member of these formations is composed of a series of strata of brownish cellular limestone interbedded with bituminous shales, but the continuity is not equivalent to that of the overlying gypsum. The sulphur-bearing formations lie in isolated basin-like deposits 1 to 5 miles long; the width varies from 1000 to 3000 ft and the thickness may reach a maximum of 200 ft. In the larger deposits, sulphur usually is disseminated through the limestone; it may lie in thin seams parallel to the bedding or may occur as well-developed crystals in the porous phases of the rock. The grade of ore as mined lies between 12 and 50 pct, the estimated average being 26 pct.^{32,72}

Distribution—The region of sulphur deposition in Sicily is confined to the south central part. The deposits are included in an area of approximately 495 square miles, constituting 5 pct of the island. There were 99 mines producing in 1939 and the 13 largest produced 70 pct of the total. Relatively important deposits, similar to the Sicilian, occur on the mainland, and the principal mines are found in the northeastern part of Italy. The mines are usually inferior to those of Sicily, yet the production before World War II reached one third of all sulphur produced by Italy.

Mining—Methods of mining and beneficiation are the most highly developed for any deposits of this type in which the ore is brought to the surface through mine openings such as shafts, tunnels, and drifts. This was brought about by the great number of years the Sicilian mines have been in operation and also by the size and extent of the deposits.^{61,62} The largest mines have installed mechanical equipment for stoping, tramming, and hoisting. Development has been carried to 1400 ft in depth with workings extending great distances from the outcrops. Where beds are flat, the room-and-pillar system is used, and after pillars have been robbed rooms are closed by waste filling or caving of the roof. The longitudinal cut-and-fill method of stoping is commonly employed in the larger mines, especially where the dip is steep. Development work is carried well ahead of extraction, and the mines can thus be worked efficiently and with high recovery. The danger of fires, particularly in the richer deposits, is a serious hazard. Hydrogen sulphide in pockets in the formation is an additional source of danger. Pumping large volumes of water constitutes a considerable item of expense.

Preparation—At one time the Calcaroni method was employed almost universally. This method employs skillfully constructed piles of ore 15 to 100 ft in diameter and 3 to 15 ft deep.⁶¹ When the ore is ignited, part of the sulphur is burned. The heat of combustion liquefies the remainder and about one half of the sulphur is recovered. The Gill regenerative furnace was developed about 1880 to improve on the efficiency of the Calcaroni and to reduce the quantity of objectionable gases. This furnace consists of a series of masonry kilns, eight being the maximum, which are arranged in circular form and connected in series by flues. The kilns are filled with ore and ignited, and the products of combustion pass successively through the remaining charged kilns before being discharged to the atmosphere. Thus the gases and vapors transfer their heat to the ore; sulphur vapor is recovered by condensation; and relatively cool gases only are wasted. The cycle is continuous and extraction of sulphur lies between 80 and 85 pct. The product, as in the Calcaroni system, is contaminated with fine gangue and analyzes from 90 to 95 pct sulphur. Other methods for beneficiation have been tried, such as concentration by flotation, solvent extraction of sulphur, and application of steam in closed containers.⁷⁵ These methods have not shown sufficient reduction in costs to displace the older systems to any great extent.

SULPHUR DEPOSITS IN MANY COUNTRIES

Deposits of sulphur are found in many countries of the world and in the aggregate contain substantial reserves. Some of these deposits are operated profitably and are of economic importance to the countries in which they are located. A considerable number are situated in isolated

regions and at high elevations. The costs for production and transportation in such cases are usually prohibitive. Most of these deposits originate by thermal activity associated with solfataras and thermal springs. The gases and solutions given off, being highly acid, have altered the formations surrounding each vent into masses of bleached, porous rock. Sulphur was deposited subsequently, both in crystalline and massive state, filling the fissures, vugs, and pores. The bleached outcrops of the altered rock indicate the presence of ore, which, because of need for oxygen to effect deposition, is usually found at shallow depths.

Distribution—The most important deposits from the standpoint of production are in the Andes Mountains of South America^{25,55,80} and in Japan.^{76,77} The Andean deposits occur at exceptionally high elevations in a zone about 3000 miles long extending through Peru and Chile. There are more than 100 deposits in this area, with indications that some of them contain substantial tonnages of high-grade ores. For the past 10 years, production has averaged about 30,000 tons annually.⁴⁹ In Japan, sulphur is found in a chain of volcanoes extending through the main islands and there are more than 40 known deposits. The principal deposits are situated on northern Honshu and Hokkaido Islands and there 12 important mines have been responsible for most of Japanese production. After World War II, production declined materially, owing to the disrupted economy of the country. This is illustrated by the yearly production figures, which range from 200,000 tons before the war to 21,000 tons in 1946.⁴⁹ There are small and scattered deposits in European⁸⁴ and Asiatic countries, as well as in the mountain ranges bordering the Pacific Ocean, including the Netherlands East Indies, the Aleutian Islands of Alaska,⁴³ the Sierra Nevada Mountains of California,^{2,42} and the numerous mountain ranges of Mexico.^{4,56} Other localities in the United States where deposits have been operated include the states of Nevada,^{1,31} Utah,³⁹ Wyoming,^{87,88} New Mexico, and the western part of Texas.⁵³

Mining and Preparation—Mining methods consist of simple forms of open-pit, gophering, room-and-pillar, and open stope-and-pillar. Melting of sulphur in autoclaves is one method of beneficiation commonly used, but recovery rarely exceeds 50 pct. Low-grade ores can be concentrated by flotation before additional treatment. Distillation of sulphur is commonly practiced in Japan and Chile by charging the ore into retorts of small capacity, which are heated externally. Usually 6 to 12 retorts comprise a unit, which is equipped with common firebox, flue, and condensation chamber.

ORIGIN OF SULPHUR

The principal deposits of the world—the salt-dome type and those of Sicily—have several features in common, which may be indicative

of their origin. In both regions, sulphur is closely associated with limestone, gypsum or anhydrite; carbonaceous matter, in the form of petroleum and petroleum residues, or as bitumen, is a frequent constituent of the sulphur-bearing rock or associated formations; and hydrogen sulphide is present as a gas or in solution in water.⁷² These common features led to the hypothesis that the sulphur was formed through reduction of sulphates by carbonaceous matter. As a result of this reaction, calcium carbonate and hydrogen sulphide were first formed, the hydrogen sulphide being subsequently oxidized to sulphur.⁶⁵ Laboratory experiments have shown that this reaction requires temperatures in excess of 1100°F, and there are no indications that such temperature existed in either type of deposits. The question arises as to whether time, measured in geologic sense, may at normal temperatures bring about reactions that in the laboratory require high temperatures. Another theory, recently discussed in various publications, does not require unusual temperatures but is based on the power of certain species of anaerobic bacteria to reduce mineral sulphates.^{8,22,90,91,92,93} These organisms derive energy from carbonaceous matter of their environment and oxygen from molecular oxygen of the sulphate minerals. According to this theory, the first product of reduction is calcium sulphide, which reacts in the presence of water with carbon dioxide, generated in the life process of the organism, to form calcium carbonate and hydrogen sulphide.³² Extensive experimental work recently conducted has demonstrated the presence of bacteria in oil-field waters in great abundance. These bacteria include sulphate-reducing forms that appear to have been instrumental in the formation of sulphur deposits associated with hydrocarbons.⁹² The oxidation of hydrogen sulphide to sulphur can best be explained by the assumption that this reaction took place where deposits were exposed to oxidizing conditions. This assumption has been made for Sicilian deposits, and there is no evidence available or recorded that would prohibit a similar consideration for the salt-dome type.⁷³

Volcanic emanations¹⁵ frequently contain sulphur vapors, sulphur dioxide, and hydrogen sulphide. Many deposits that outcrop at the surface have evidently originated from one or more of these gases. Temperatures are prohibitively high at the seat of activities for deposition, but at more remote locations, or during dying stages of volcanism, lower temperatures are more favorable. There are three methods by which sulphur may be deposited from solfataras: the first by condensation of sulphur vapors, the second by reaction between hydrogen sulphide and sulphur dioxide, and the third by oxidation of hydrogen sulphide. Deposits may originate also by deposition of sulphur from thermal springs containing hydrogen sulphide. Other agents of deposition,³² active in mineral springs, are sulphur bacteria, which have the power of

oxidizing hydrogen sulphide to sulphuric acid and, in an excess of the gas, of storing sulphur in their cells.

PYRITES

Definition—Pyrites is an inclusive term used to designate metallic sulphides such as iron pyrites (pyrite), magnetic pyrites (pyrrhotite), white iron pyrites (marcasite), copper pyrites (chalcopyrite), and tin pyrites (stannite). The metallurgical treatment of some of these and other sulphide minerals in the copper, lead, and zinc industries frequently results in the recovery of by-product sulphur in some form. The term "pyrites" is here limited principally to sulphide minerals in which sulphur is of primary interest. The minerals of common commercial interest under this definition are pyrite, pyrrhotite, and marcasite.

Properties—Pyrite (FeS_2) when pure contains 53.4 pct S and 46.6 pct Fe. It has a brass-yellow color, metallic luster, greenish or brownish black streak; and crystals of cubic, octahedral, pyritohedral, or other isometric forms are common. The hardness is from 6.0 to 6.5 and the specific gravity 4.9 to 5.2. It has no cleavage, is brittle, and of uneven fracture.¹⁶

Pyrrhotite, varying in chemical composition, is considered to have the formula $\text{Fe}_{11}\text{S}_{12}$ and when pure contains 38.4 pct S and 61.6 pct Fe. It is bronze in color, has metallic luster and black streak. Usually it occurs in a massive form but occasionally in tabular or pyramidal crystals of the hexagonal system. Its hardness is from 3.5 to 4.0 and it has a specific gravity of 4.5 to 4.6. It is brittle, of uneven fracture, and is magnetic.

Marcasite has the same chemical composition and hardness as pyrite. The luster is metallic, the color ranges from pale yellow almost to white, and the streak is greenish black. It is sometimes found in tabular crystals of the orthorhombic system, also frequently in radiating fibrous masses, and its multiple twinning often results in jagged outlines. It is brittle, of uneven fracture, and has a specific gravity of 4.85 to 4.90.

Origin—Pyrite and pyrrhotite are very common sulphide minerals and are associated with rocks of all ages and types. A discussion of their origin here is necessarily limited to relatively pure deposits. The origin of such deposits is generally ascribed to their association with igneous rocks.⁴⁰ Literature on the subject indicates that the origin is dissimilar in other respects and divides these deposits into two broad groups—those formed at high temperatures and those formed at intermediate temperatures. Associated minerals are used as evidence of the temperature at which deposition took place. Pyrrhotite deposits and those associated with silicates were formed at relatively high temperatures and at great depths. This class includes deposits of magmatic origin, those of the con-

tact-metamorphic type, and those believed by many to have resulted from the injection of sulphide magmas. The second group, those formed at intermediate temperatures, includes deposits associated with minerals such as calcite, barite, and quartz. Deposits of this type may have been formed by hydrothermal replacement at moderate depths, and the origin of deposits in Spain has thus been explained.^{9,83}

Pyrates Deposits

UNITED STATES

Deposits are being operated in Tennessee, New York, Virginia, California, Wisconsin, Montana, Illinois, Indiana, and Pennsylvania. The principal production is from the Ducktown region, in the most southeasterly corner of Tennessee, which is currently leading all other states in production. Coal brasses are recovered by concentration in the treatment of certain coals, particularly in Illinois and Indiana.

Formations—The Ducktown district lies in the southern Appalachian Mountains. The formations are of Lower Cambrian age, and consist almost wholly of metamorphosed conglomerate sandstone and shale, complexly folded and faulted. For many years, it was assumed that the ore bodies were the result of partial replacement of included beds of limestone and marble.¹⁹ Later investigation resulted in the theory that the deposits were formed by several stages of mineral deposition, each initiated by fault movements and each associated with a distinct group of minerals. Ore minerals were last in the order of deposition and replaced most of the vein material and portions of the country rock.⁶⁰ The ore bodies are elongated, roughly tabular masses, some of which are curved, folded or lens shaped. In general, the veins strike northeast and dip from 35° to 65°. In length they extend over a distance of about 2000 ft and in width from a few feet to a maximum of 180 ft. The ore consists of massive pyrrhotite, pyrite, and chalcopyrite, with minor amounts of sphalerite and galena. The principal gangue minerals are quartz, actinolite, and tremolite. The ore contains from 25 to 39 pct S, 35 to 45 pct Fe, and 0.8 to 2.5 pct Cu.

Mining—The ore is mined by sublevel stoping.^{46,35} Longitudinal stopes are taken out from wall to wall where the ore is not wider than 40 ft. In wider sections, transverse stopes 40 ft wide alternate with pillars of equal thickness. The ore, when broken in stopes, falls to funneled raises and is then worked through grizzlies into cars on the haulage level. After tramming to ore pockets or directly to skips, it is hoisted to the surface through an inclined or vertical shaft generally located in the footwall.

Preparation—Copper originally was the principal value in the Ducktown ores. Sulphur subsequently became of increasing importance because of the strategic location. The major part of the ore, usually low

in copper, is floated to produce copper and pyrites concentrates. The latter is roasted in multiple-hearth furnaces and sulphur dioxide is sent to the chamber or contact acid plants for production of sulphuric acid. Calcines from the roaster are sintered and shipped to Birmingham for conversion to pig iron and steel. Zinc is recovered as a 50 pct zinc concentrate and is sold as such.

CYPRUS

Deposits of cuprous pyrites on Cyprus were worked for copper in very ancient times. An American company, Cyprus Mines Corporation, began an exploration program in 1914. Two massive sulphide ore bodies were discovered and production started in 1922. It has been continuous since that year, except for the suspension of operation caused by World War II. Shipment of pyrites amounted to 523,574 tons in 1938 and 263,314 tons in 1946. The ore bodies are found in a narrow zone of andesitic lavas that lies as a rim around the island's principal mountain mass of diabase and serpentine. They occur as irregular lenses and stockworks of massive and disseminated ore. Copper as chalcopyrite and chalcocite is the principal nonferrous metal and small amounts of zinc, gold, and silver also are present. Two large, massive ore bodies are now being mined—the Skouriotissa and the Mavrovouni. The Skouriotissa is a horizontal lens 2000 ft long by 600 ft wide. The thickness ranges from a few feet near the perimeter to 150 ft in the center. The ore averages 2.25 pct Cu, 48.0 pct S and 43 pct Fe. The Mavrovouni ore body is a large, irregularly inclined chimney enclosed in hydrothermally altered lava. The ore averages 4.2 pct Cu, 48 pct Fe, 0.4 pct Zn, 0.025 oz Au and 0.25 oz Ag. A top-slicing system of mining as developed by the company is used where conditions are favorable. Methods of treatment differ for the two ore bodies and are described in detail in recent publications.^{11,12}

SPAIN

Postwar information on deposits of pyrites in European countries is not complete. The following discussion is therefore based primarily on prewar operations. The zone of pyrites deposition that extends through the province of Huelva in southern Spain and into Portugal has furnished the major part of the world's supply for many years.^{33,34,83} World War II curtailed production and exports, as shown by recent production figures, which were 792,587 tons in 1946, compared with 2,727,003 tons in 1939.

Formations—Formations in the vicinity of the deposits consist of folded slates and graywacke, striking east and west, and probably of Carboniferous age. After being folded, the slates, which dip steeply northward, were intruded by porphyries and diabase. The ore bodies are found in the form of elongated lenses in these formations or at

the contact of intrusive rocks. There are approximately 50 such lenses, the maximum dimensions of which are: length, 6000 ft; width, 800 ft; known depth, 1800 ft.⁵⁷ Massive pyrite is frequently found in well-defined contact with the enclosing rock and in some places a transition zone of disseminated pyrite occurs. The ore contains minor amounts of chalcopyrite, sphalerite, and galena. The small amount of gangue consists of quartz with some barite. The total reserves of pyrite ores in Spain have been estimated at approximately 500,000,000 tons.

Mining—The two principal producers in this district are the Rio Tinto Co. Ltd. and the Tharsis Sulphur and Copper Co. Ltd. The ore body in the San Dionisio lode, operated by Rio Tinto Co. Ltd., has approximate dimensions of: width, 600 ft; length, 3300 ft; and depth, 1200 ft. The original opencut resulted in a terraced crater of which the rim is about 1350 by 1800 ft and the depth 450 ft. Some mining is still being carried on by glory-hole methods in the open pit. The ore is scraped into winzes, which feed loading pockets on the twenty-third level. Thence it is trammed by compressed-air haulage, hoisted electrically in skips to the sixteenth level, and hauled by electric locomotives through a 3-mile adit to the surface. Underground methods formerly consisted of driving wide drifts and crosscuts on approximately 40-ft centers with 45-ft vertical intervals between the levels. The present underground system, accounting for the major production, consists of mining the entire block of ore between the old filled stopes by driving sublevels 9 ft apart across the ore body. From these sublevels, the ore is broken out in blocks 9 ft square. Timber and lagging are used in all workings, the timbers being subsequently removed and the stopes filled with waste. Good ventilation and removal of all timber are necessary on account of the danger of fire. Ore from underground workings is dropped through passes to the sixteenth level, where it is hauled through the adit to the surface.

Preparation—Ore averaging 48 pct S and less than 1.5 pct Cu is marketed with no treatment other than screening. Ore containing more than 1.5 pct Cu is leached for its copper content before shipment. For leaching, the ore is placed in huge piles, which are intermittently sprayed with water for two or more years. The solution is collected and passed through launders containing scrap iron to precipitate the copper. After leaching, the ore analyzes from 48 to 50 pct S and 0.4 pct Cu. Ores containing 3 pct Cu or more are smelted for recovery of copper. Sulphur is produced from ore of this grade by methods similar to the Orkla process in Norway.

NORWAY

Pyrites production comprises the major mining industry in Norway and is also the principal source of copper.³⁴ Production declined from

1,027,776 tons in 1938 to 247,465 tons in 1945. In 1946, the production was 537,916 tons. Important deposits are found in the Hardanger, Trondheim, Grong, and northern districts. The Lokken mine, operated by the Orkla Mining Co.,⁵⁹ with a smelter at Thamshavn, is the major producer of pyrites.

Formations—The Lokken deposits are in the Scandinavian mountain chain and the country rock is described³³ as schistose greenstone with gabbro intrusions on the hanging wall a short distance from ore. The main ore body is lens shaped; it dips at an angle of 45° , has a thickness of 150 ft in the central part and a length of approximately 6000 ft. The principal mineral is medium-grained pyrite and quartz is present in small amounts. The ore averages 42 pct S and 2.5 pct Cu.

Mining and Preparation—Shrinkage stoping is the system used for mining. After crushing and screening, the major part of the production is shipped to Scandinavian pulp mills or European acid plants. The calcines are retained by the producer or shipped to others for recovery of copper and utilization of iron. The Orkla process for recovery of sulphur and copper is used with another part of the production. A charge consisting of ore, coke, quartz, and limestone is smelted in a blast furnace. The resulting gases contain, in addition to sulphur vapor, sulphur dioxide, carbon disulphide, and carbon oxysulphide.⁵⁹ These gases react in the presence of a catalyst to form more sulphur vapor, which is condensed to a liquid and solidified. Copper matte is converted to blister copper.

SWEDEN

For many years, the Boliden Mining Co. has been the major producer of pyrites in Sweden. Total production for the country in 1947 was 386,000 tons. The ores are complex and contain pyrite, chalcopyrite, arsenic, bismuth, selenium, gold, and silver. Selective mining is employed to produce pyrite ores and ore of high gold content. Treating methods formerly included roasting and smelting with recovery of elemental sulphur from stack gases by an absorption process. Complicated metallurgical processes were used for the recovery of other contained metals. Selective flotation with recent improvements now produces clean pyritic concentrates, which can be sold to pulp mills. These developments have made possible the gradual suspension of unprofitable recovery of sulphur from stack gases. Lower production recently at the Boliden mine has been offset by development of new deposits of pyrites in the vicinity.

Elemental sulphur is recovered as a by-product from oil-shale plants that were installed by the Swedish Government during the recent war. Approximately 15,000 tons of sulphur a year is thus recovered.

FINLAND

Production of cuprous pyrite concentrates by the Government-owned mine, Outokumpu,¹³ has reached an annual rate of 177,000 tons since the war. The smelter, formerly operated at Imatra, was moved to western Finland. Outokumpu concentrates are now mixed with nickel-copper concentrates from the Nivala deposit for smelting at the new location. The production of liquid sulphur dioxide at Imatra has been discontinued and sulphur dioxide in stack gases is now converted to sulphuric acid.

OTHER PYRITES DEPOSITS

Japan, normally a large producer of pyrites, uses its entire output in the manufacture of acid. Italy, another main producer, is similar to Japan in that its production is principally for local consumption. Iron in the calcines is an important factor where iron ores are scarce. Other important sources of pyrites are Russia, Germany, Greece, France, Portugal, and Canada. Countries in which minor amounts of pyrites were produced before World War II include Korea, Yugoslavia, Czechoslovakia, Union of South Africa, Algeria, Australia, Poland, Southern Rhodesia, Rumania, and the United Kingdom.

MARKETING AND USES

The largest single use of sulphur is for the production of sulphuric acid. Native sulphur, pyrites, smelter gases, particularly from zinc concentrates, and hydrogen sulphide are all used for this purpose. The manufacturer of sulphuric acid, therefore, has his choice among these raw materials. His selection will be determined by economic factors such as price, availability, and dependability.²⁰

Sulphur and sulphuric acid enter into a vast number of industries and a multiplicity of uses, some of which are shown in Fig 4.^{18,45} Washed phosphate rock is treated with sulphuric acid in the preparation of fertilizers. This not only makes the phosphate available to plants but also furnishes sulphur, which is an essential plant food. In petroleum refining, sulphuric acid removes gums and tarry matter, as well as other constituents that would form end products of a corrosive nature. Sulphuric acid in recent years has become increasingly important in synthesizing fuels and chemicals from petroleum. A specific example recently developed is the manufacture of high-octane components for aviation gasoline. Nitrogenous constituents resulting from the coking of coal pass off as ammonia and the gases are scrubbed with sulphuric acid to produce ammonium sulphate. Sulphuric acid is used in the purification of other products of coal distillation, such as benzol and toluol. The iron and steel industry uses sulphuric acid to remove scale formed during the various steps of rolling and annealing. Another

metallurgical operation consuming sulphuric acid is electrolytic production of zinc. A large and increasing use in the paint and pigment industry is for manufacture of titanium dioxide. The ore is dissolved in sulphuric acid and titanium dioxide is then precipitated in a pure form by hydrolysis. Among the explosives, black powder with sulphur as a constituent has been almost entirely replaced by nitroglycerin in the

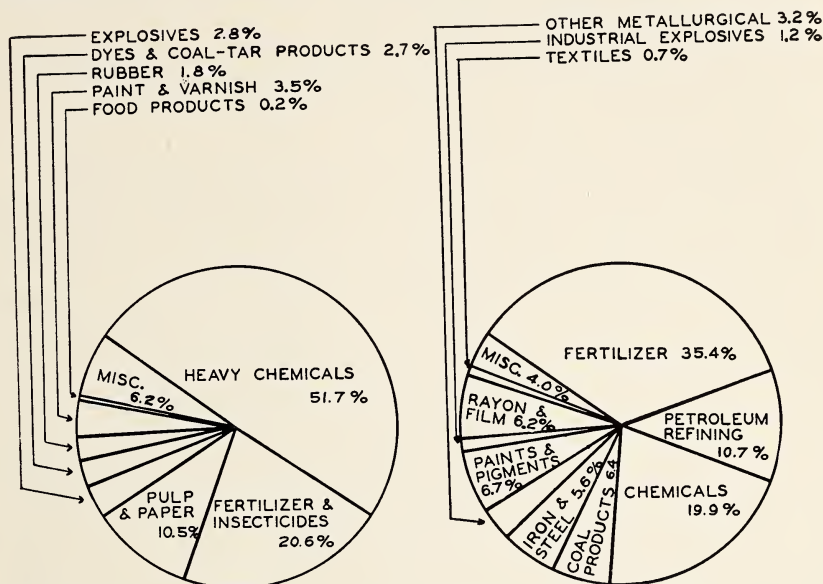


FIG 4—DISTRIBUTION BY INDUSTRIES OF (LEFT) SULPHUR AND (RIGHT) SULPHURIC ACID USED IN THE UNITED STATES IN 1947.

From figures assembled by *Chemical Engineering*.

form of dynamite and similar compounds. In the manufacture of nitroglycerin, nitration is carried out with nitric acid in the presence of concentrated sulphuric acid. Propellant explosives for military use contain large amounts of nitrocotton, which is made by nitrating cellulose in a bath of mixed nitric and sulphuric acids. In the viscose process for making rayon, the viscose solution is precipitated in a sulphuric acid solution. Sulphur is employed in the viscose process in the form of carbon bisulphide, this being used to make cellulose xanthate from caustic soda and cellulose. Large amounts of sulphuric acid are used in the nitrating bath in making nitrocotton from which motion picture films are produced. The textile industry uses sulphuric acid in the various operations of washing, bleaching, shrinking, and dyeing. Sulphur and sulphur dioxide are used in the production of magnesium ingots and castings to create an inert atmosphere.

As in the manufacture of sulphuric acid, either sulphur or pyrites may be used as a raw material for the production of sulphite pulp. In

this process, a solution containing calcium bisulphite and sulphurous acid is prepared by absorbing sulphur dioxide in a solution of milk of lime, or by a reaction between sulphur dioxide and lime rock in towers. The resulting solution digests the wood chips until most of the noncellulosic materials have been dissolved. In many kraft plants, sulphur is added to the cooking liquor to increase the sulphidity for the production of high-strength paper.

The amount of sulphur used for the manufacture of rubber depends upon the properties desired in the final product. Hard rubber in storage-battery cases usually contains 30 pct while rubber used in tire stock may contain not more than 1.5 pct. Sulphur is essential also in the manufacture of synthetic rubbers, which have more resistance to chemical attack and oil deterioration than natural rubber. Thiokol, one of the special-purpose rubbers, results from the chemical reaction between ethylene dichloride and sodium polysulphide.

Sulphur and sulphuric acid are assets of great and expanding value in agriculture. Work on insecticidal and fungicidal uses of sulphur is currently in progress in experiment stations and research organizations. Sulphur, in the form of dust and also in the form of spray materials, such as lime sulphur solution and wettable sulphurs, is used in control of pests that attack fruit trees as well as field and truck crops. The development of combination contact insecticides in which sulphur is mixed with such materials as DDT, pyrethrum and rotenone, is of particular interest. Sulphur and sulphuric acid are used as soil amendments to neutralize alkalinity and to correct sulphur deficiency. Where soils contain a relatively high concentration of selenium, together with a deficiency in sulphur, selenium may be selectively absorbed by certain forms of plants and cattle may be thus poisoned. When added to such soils, sulphur acts as an inhibitor to absorption of selenium. Sulphur in the form of sulphur dioxide is used in greenhouses and mushroom houses as a fumigant. Carbon bisulphide is used to exterminate insect pests in soils and as a weed killer.

TESTS AND SPECIFICATIONS

Specifications for sulphur and pyrites concern three items of principal interest: (1) that the raw material shall contain a guaranteed minimum of sulphur; (2) that it shall contain not more than specified amounts of injurious materials; and (3) that not more than certain amounts of materials that prevent or retard combustion shall be present.

Sulphur produced by the Frasch process frequently averages 99.8 pct. It is guaranteed to contain not less than 99.5 pct S on a dry basis and to be practically free of arsenic and selenium. Impurities consist

of traces of ash and petroleum hydrocarbons. Italian sulphur is sold under several different grades as a result of the varying amounts of inorganic impurities.

Commercial flour sulphur is prepared by grinding and sizing crude sulphur, and the chief specification for this material, in addition to those listed above, relates to particle size. Commercial flour sulphur is used by the rubber industry. In addition to being carefully sized, it should contain not more than 0.01 pct free acid. Flowers of sulphur is a finely divided product manufactured by subliming crude. It contains a variable amount of amorphous (insoluble in carbon bisulphide) sulphur.

Sulphurs as marketed are customarily tested for moisture, ash, sulphur, organic impurities and free acid to ensure proper specifications. Moisture and ash are determined by standard methods. Dry sulphur is extracted by carbon bisulphide and the sulphur content is determined by subtracting the insoluble portion from 100. When amorphous sulphur is present, hot aniline can be used as an additional solvent. Organic material is generally determined by burning a small sample under controlled conditions and comparing the resulting deposit of carbon with a series of standards. Free acid is determined by wetting a ground sample with alcohol and extracting the acid with water, subsequently titrating the extract with standard caustic solution.⁶⁶

Because injurious impurities are commoner in pyrites than in sulphur, specifications are more rigid. Specifications for pyrites are usually determined by agreement under long-term contracts between the producer and consumer, because each mine produces ore peculiar to itself. Physically, pyrites is classed either as lump or fines. Lump ore varies in size from 2 to 10 in. and should contain not more than 10 pct through $\frac{1}{2}$ or $\frac{3}{8}$ -in. screen. The undersize, classed as fines, was sold at a discount prior to development of suitable burners. Contracts usually call for a premium or penalty when the sulphur content deviates from a guaranteed percentage. Zinc and lead are objectionable because they cause retention of sulphur in calcines. For the manufacture of sulphuric acid, more than 1 pct of arsenic is objectionable, and the rigidity of this specification depends on the type of equipment available at consumers' plants for removal of arsenic from the gases. Where pyrites is to be used for papermaking, selenium may cause oxidation of the sulphur dioxide to sulphur trioxide in the digester, and is therefore objectionable. The calcines, which may contain other valuable constituents, are disposed of by agreement between producer and consumer.⁶⁹

Test methods employed are the usual standard methods for determination of sulphur, iron, copper, zinc, lead, arsenic, selenium, and moisture.⁶⁶

POLITICAL AND COMMERCIAL CONTROL

The present status of the world sulphur industry can be clarified by a review of major developments during the past 45 years. In the early part of the twentieth century, the Frasch process made rapid strides commercially, supplanting Italian and Japanese sulphur in American markets and exporting small amounts. Subsequent to World War I, with a greatly increased production and with previously scarce shipping facilities then available, American sulphur gained rapidly in all world markets. During the first World War, domestic manufacturers of sulphuric acid had difficulty in obtaining pyrites from foreign sources and many plants were altered to burn sulphur. There has been no subsequent change in the attitude of American consumers, because domestic sulphur offers greater security in supply. After World War I, American producers, in order to develop additional outlets, found it necessary to enter foreign markets more aggressively, and in 1922 the Sulphur Export Corporation was formed to distribute sulphur in world markets.

Many nations of the world have fostered local sources of production by bounties, tariffs, embargoes, and sometimes by complete government control. In 1935, the Italian Government established a fund of 20 million lire to underwrite the price it guaranteed to Italian producers of sulphur. Similar subsidies continued until the outbreak of World War II. Since that time, Italian production has been insufficient to supply appreciable amounts for export and therefore subsidies have not been feasible. In 1948, trade agreements between the French and Italian Governments have made possible the exportation of about 80,000 tons from Italy. Japan protected its industry prior to 1941 by a 20 pct duty on the c.i.f. price of imported sulphur. Japan does not export any sulphur at this time. In 1934, the Spanish Government practically prohibited imports of sulphur into Spain, in order to protect a new plant that was built to produce sulphur from pyrites. The plant was not able to supply all of Spain's requirements and accordingly some sulphur was imported under governmental control. Through a Government agency known as Mining Credit Institute, Chile is authorized to pay a subsidy of 100 pesos per ton of refined sulphur exported. In Finland, a Government-owned pyrites mine, having a productive capacity of 400,000 tons per year, sells pyrites concentrates to Scandinavian paper mills. In Sweden, a Government-owned shale-oil recovery plant has produced sulphur as a by-product since 1943. In 1947, it sold 14,000 tons in the domestic market. In Portugal, a plant for producing sulphur from pyrite with a capacity approximately equal to Portugal's consumption is protected by an import tax on sulphur. The British Government controls the purchase and distribution of sulphur and pyrites to manufacturers of sulphuric acid in England and

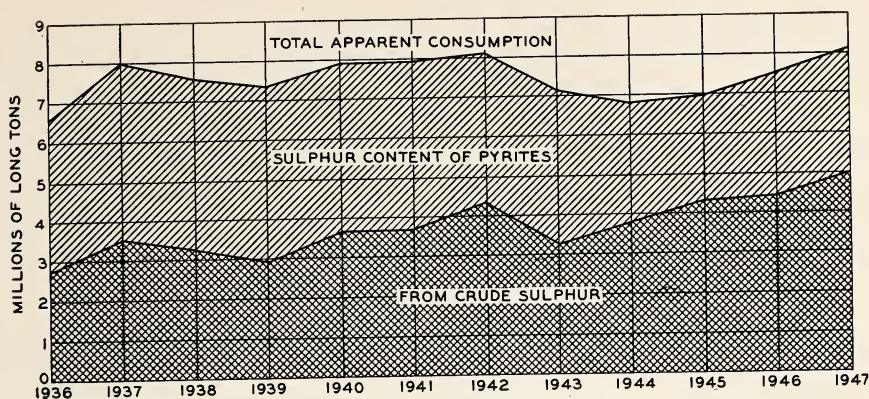


FIG 5—WORLD CONSUMPTION OF SULPHUR FROM CRUDE SULPHUR AND PYRITES.

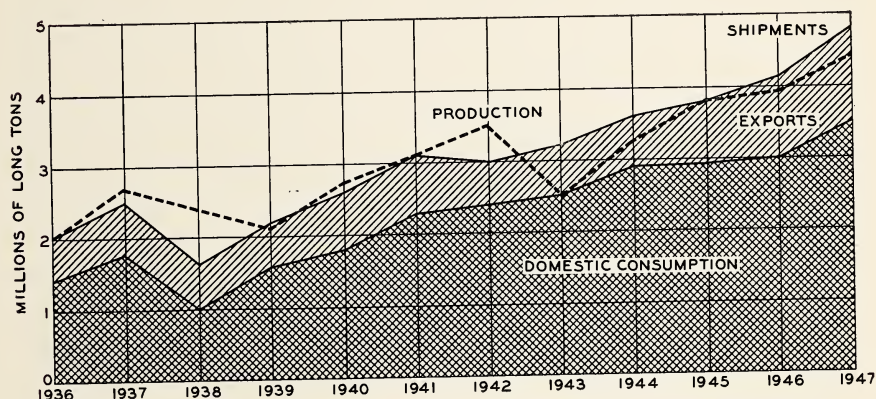


FIG 6—PRODUCTION AND SHIPMENTS OF CRUDE SULPHUR, UNITED STATES.

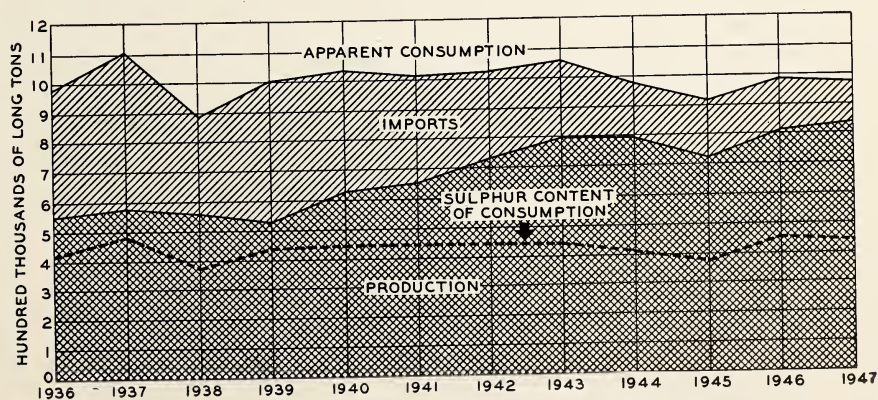


FIG 7—DOMESTIC CONSUMPTION OF PYRITES, UNITED STATES.

thereby effectively directs the supplies into desired channels. The Argentine Government requires importers of sulphur to purchase a percentage of their annual requirements from a domestic producer at prices considerably higher than the cost of imported sulphur. Since sulphur is not produced in Australia, the Government pays a premium of 36 shillings for each ton of sulphur recovered from sulphide ores in the form of sulphuric acid. Other countries have import duties on crude sulphur, not to protect the domestic industry but as a source of revenue.

CONSUMPTION AND PRODUCTION

Statistics and trends of the sulphur industry are illustrated by Figs 5 to 7. The part played by sulphur and pyrites, respectively, in supplying the world requirements for sulphur in all forms is shown in Fig 5. The adjustment of domestic production to shipments since 1935 is illustrated in Fig 6, which also shows the failure of exports to increase comparably with domestic consumption in recent years. Increasing domestic production of pyrites is shown by Fig 7. World trade relations for the two minerals emphasize the fact that, under present economic conditions, the United States relies on crude sulphur and Europe on pyrites as the principal source of sulphur.^{48,49} This situation is essentially true today but the economic dislocations in many foreign countries caused by the war have resulted in a decline in world production of pyrites and an increased demand for American sulphur from other countries.

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CHAPTER 48

TALC AND GROUND SOAPSTONE*

BY A. E. J. ENGEL†

INDUSTRIAL talcs and ground soapstones both include earth materials of different chemical and mineral compositions. In general, the industrial talcs are composed of silicates that contain appreciable amounts of magnesia. Generally talc, the mineral, is a predominant or at least common constituent. Talc, the mineral, is a hydrous magnesium silicate, with a suggested theoretical formula $\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$ or $\text{H}_2\text{O} \cdot 3\text{MgO} \cdot 4\text{SiO}_2$, which postulates 63.5 pct SiO_2 , 31.7 pct MgO , and 4.8 pct H_2O .¹¹ Actually different single grains or leaves of pure talc have variations in water content ranging from 3.5 pct to more than 7 pct, as well as slight differences in the proportions of MgO and SiO_2 .¹⁶

Only a very small percentage of the ground industrial talcs produced in the United States approaches the composition given above (see Table 1). The purer talcs invariably occur as alteration products of magnesium carbonate rocks. Some of these relatively pure talcs include compact, massive types largely mined in California, which are designated as steatite.^{38,56} In general, steatites cannot contain in excess of 1.5 pct CaO , 1.5 pct combined FeO and Fe_2O_3 , and 4 pct Al_2O_3 . The less pure varieties of massive talc and mixtures of magnesian silicates are commonly called soapstones, or merely talc.

Many industrial earth products classified as talc or as soapstone contain a variety of minerals, especially serpentine ($\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9$), chlorites (hydrous magnesium, iron, aluminum silicates), tremolite ($\text{Ca}_2\text{Mg}_5\text{H}_2[\text{SiO}_3]_8$), anthophyllite ($[\text{MgCa}]\text{SiO}_3$), diopside ($\text{CaMg}[\text{SiO}_3]_2$), and quartz (SiO_2). The carbonates calcite (CaCO_3), dolomite ($\text{CaMg}[\text{CO}_3]_2$), and magnesite (MgCO_3) are also present in some industrial talcs and soapstones.

Some of these minerals, as well as sulphides, sulphates, and iron and manganese oxides, if present at all or in excess of minute amounts, may alter the composition of the industrial talc sufficiently to restrict materially its use or to lower or destroy its value. These factors are discussed in a subsequent section of this chapter.

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† U. S. Geological Survey, Washington, D. C., California Institute of Technology, Pasadena, California.

Other minerals, especially some silicates, may impart a chemical composition and other properties highly desirable for a specific industrial use. An example of this type is the highly tremolitic "talc" of New York state and California, some of which may contain 50 pct or more of tremolite and less than 25 pct of the mineral talc, but have a CaO content of about 4 to 6.5 pct, a CaO:MgO ratio of about 1:4, excellent color, and fibrous character ideally suited for use in paints and in certain ceramic bodies.^{27,28}

PROPERTIES

Industrial talcs of various kinds are employed where certain of the following properties are desired: extreme whiteness, a high degree of softness and smoothness, fibrous or flaky forms of components with large surface areas in relation to their mass,⁴⁰ excellent coverage, good luster or sheen, high "slip" or lubricating power, specific types of oil and grease absorption, chemical inertness, high fusion point, low shrink-

TABLE 1—*Chemical Analyses of Industrial Talcs Mined in the United States*

Constituent	1	2	3	4	5	6	7
	Composition, Pct						
SiO ₂	59.80	66.23	56.33	41.02	61.35	39.54	59.61
Al ₂ O ₃	0.57	1.05	3.19	4.23	4.42	3.72	1.65
Fe ₂ O ₃	0.05	0.13	} 5.39	} 5.85	} 1.68	3.62	} 0.92
FeO.....	0.15	0.22				7.12	
MnO.....	0.39	0.16	0.11			1.60	
CaO.....	6.80	2.26	0.41	4.76	0.82	5.93	0.84
MgO.....	27.45	25.71	27.89	28.60	26.03	24.84	30.01
Na ₂ O + K ₂ O.			0.87			0.08	0.26
SO ₃	0.07	0.01					
Ign. loss.....	4.75	3.86	} 5.68	} 15.51	5.10	5.04	} 5.94
Water (105°).	0.45	0.25				0.02	
CO ₂	1.18	0.56	0.36			9.50	
Total.....	101.66	100.84	100.23	99.97	99.40	100.91	99.23

1. Analysis of average sample of mined talc zone, Talcville, Gouverneur district, N. Y. Analyst Glen Edington, U. S. Department of Agriculture.

2. Analysis of average sample of mined talc zone, Fowler, Gouverneur district, N. Y. Analyst Glen Edington, U. S. Department of Agriculture.

3. Talc of Vermont, Vermont State Geological Survey.

4. White talc from Murray County, Georgia. Analyst L. H. Turner, Georgia Department of Mines, Mining and Geology.

5. Talc from Hewitt mine, North Carolina. Analysis from *Economic Paper* No. 3, Geological Survey of North Carolina.

6. Massive talc from Schuyler, Virginia. Analyst R. B. Ellestad. From H. H. Hess.²⁹

7. Steatite-grade talc from the Talc City mine, Inyo County, California. Analysis from Sierra Talc Co., in Page.⁴⁶

age, low electrical and thermal conductivity, good retention as fillers, high specific heat, and resistance to heat shock.

Pure talc is intrinsically a white to silvery white or somewhat greenish mineral,¹¹ which grinds white. It has a hardness of 1 to 1.5 in the Mohs scale, a specific gravity of about 2.75, perfect basal cleavage, and a greasy feel. The pure mineral is relatively inert and remains undecomposed in contact with acids. When talc is heated, a part of the water commonly present can be driven off without any change in the optical or crystalline properties of the mineral. Ewell and associates¹⁵ report that water in excess of one molecule is driven off at temperatures between 380° and 500°C. Between 800° and 840°C, the combined water of crystallization is lost, and talc dissociates into enstatite and amorphous silica. This is an endothermic reaction. On continued heating, the enstatite inverts gradually to clinoenstatite and the amorphous silica inverts to cristobalite, both mineral changes reaching completion before a temperature of 1300°C is reached. Other investigations of the constitution and thermal decomposition of talcs are noted and discussed briefly by Thurnauer and Rodriguez.⁵⁷

Detailed equilibrium relations between the crystalline phases talc, serpentine, forsterite, enstatite, and silica, and the fluid phase up to 900°C and 30,000 psi are being investigated by Bowen and Tuttle.⁴ Phases of the synthesis of talc and serpentine at temperatures up to 600°C have been studied by Jander and Felt.³³

The crystal structure of talc is very similar to that of pyrophyllite ($\text{H}_2\text{Al}_2[\text{SiO}_3]_4$).⁵⁵ The somewhat similar physical and optical properties of these minerals have caused some confusion in their identity.

They are reported to have the same space group $C \frac{6}{2h}$ with the unit cell for talc containing four molecules of $\text{Mg}_3\text{Si}_4\text{O}_{10}$.²⁵ Because of these similarities, talc and pyrophyllite are used for about the same purposes in some industries.

The indices of refraction of pure talc are $\alpha = 1.539$, $\beta = 1.589$ and $\gamma = 1.589$. The 2V is small and variable.

Few bodies of talc of minable size are devoid of either associated minerals or exotic organic and inorganic stains. Many of the associated minerals, especially silicates and even small amounts of quartz, offer no impediment to certain industrial uses, if the proportions of these minerals can be kept nearly constant over long periods of production. The associated substances necessarily alter the properties of the industrial talc in ways objectionable to some consumers, however, as will be noted under the section on Tests and Specifications.

Industrial talcs are ground from rocks ranging widely in grain size from coarse to cryptocrystalline; the component talc and other minerals may be foliated, granular, or fibrous. The fibrous and foliated forms of

the talc are commonly related to cleavages and partings and persist after the finest grinding (Figs 1a, 1b).

OCCURRENCE AND DISTRIBUTION

Most talc and soapstone deposits of commercial importance occur in altered ultrabasic igneous rocks and in metamorphosed dolomitic lime-



FIG 1a—PLATY OR SCALY TALC PRODUCED BY GRINDING COARSELY CRYSTALLINE FOLIATED TALC F AND ACCESSORY SERPENTINE S.

Gouverneur district, New York. Reflected light, $\times 20$.

FIG 1b—HIGHLY FIBROUS "TALC" PRODUCED BY GRINDING TALCOSE ANTHOPHYLLITE.

Fibrous anthophyllite has replaced bladed tremolite. Part of the anthophyllite subsequently altered to talc, which is pseudomorphous after the anthophyllite. Gouverneur district, New York. Reflected light, $\times 20$.

stones. Rocks of these types, with included talc deposits of various ages, are characteristically found in metamorphic rocks in many parts of the world.

The formation of large bodies of talc and its associated hydrous magnesium minerals, especially serpentine, from susceptible magnesium-

bearing carbonate sedimentary rocks and igneous rocks may have been accomplished largely by the action of dilute aqueous solutions. These solutions had their source, or at least the source of much of their heat, in bodies of granitic igneous rocks that were in the process of intrusion or consolidation.

Commonly the geologic environment is one of regional metamorphism, and the alteration of appropriate rocks to talc was a late or final retrogressive stage (of lowered temperature and pressure). Conditions of mild or moderate stress may have existed in the rocks as the hydrothermal metamorphism to talc occurred. Actually stress seems to have been important chiefly in producing zones of fracture and shear along which the aqueous solutions permeated and altered the rock. There is little or no evidence in most deposits that development of talc is largely dependent upon stress or greatly facilitated by it. Much talc clearly has formed in a nearly static environment, subsequent to any major deformational preparation of the rocks for the mineralizing solutions.

Most ultrabasic rocks have undergone serpentinization or steatization (the formation of talc) or both processes, so some talc or other talc-like hydrous magnesium silicates are almost invariably found with these rocks. The formation of talc from ultrabasic rocks climaxes a series of mineral alterations that take place in a wet system. Hess²⁹ describes the mineral alteration of a peridotite (olivine + pyroxene) → actinolite → chlorite → talc + carbonate rock, from an occurrence at Schuyler, Virginia, and notes that during the whole course of the alteration little has been added to the rock except H₂O and, in the very last stages, CO₂.

Commonly both serpentine and talc are formed by alteration of an ultrabasic rock, however, and in most deposits talc replaces the serpentine. Hess concluded that in deposits of this type in eastern North America the serpentine formed as an automorphic alteration of the ultrabasic rock; i.e., by action of solutions whose source was in the ultrabasic rock itself.³⁰ In these deposits, the subsequent formation of talc may be unrelated to serpentinization and attributable to hydrothermal solutions possibly derived from granite intrusives at depth.

Most carbonate sedimentary rocks in which talc deposits occur apparently have contained appreciable quantities of magnesia in the form of dolomite or other magnesium-bearing carbonates. In some of these rocks, silica is also present as an initial sediment in sandy or cherty layers. In such siliceous dolomites, a limited amount of talc could form at appropriate temperatures if sufficient water were available to satisfy the requirements for the composition of talc (Table 2). Thus the magnesia in the dolomite could react with the sedimentary silica and water to form talc. Obviously large volumes of calcite and CO₂ would be released as by-products of this reaction and a considerable decrease in

volume would result. Presumably the water would have to be derived largely from igneous sources, or ground water heated by cooling igneous rocks.

In most talc deposits there is evidence that considerable silica as well as water has been introduced, or at least widely redistributed. In some of the deposits of California, at Natural Bridge, New York, and elsewhere, the original rock now replaced by talc appears to have been initially a limestone, low in both magnesia and sedimentary quartz. In these deposits, and probably in many others, appreciable volumes of magnesia also have been introduced, or at least widely redistributed by aqueous solutions. The sources of the magnesia and silica added were either intrusive magmas or, more probably in most places, siliceous magnesian rocks at depth traversed by ascending hydrothermal solutions.

TABLE 2—*Approximate Composition of the Minerals Common in Industrial Talc*
IN TERMS OF PERCENTAGE OF OXIDES

Mineral	CaO	MgO	Al ₂ O ₃	SiO ₂	CO ₂	H ₂ O
Quartz.....				100		
Calcite.....	56				44	
Dolomite.....	30	22			48	
Magnesite.....		48			52	
Diopside.....	26	18		56		1.5-2.3
Tremolite.....	13	28		57		1.5-2.2
Anthophyllite.....	2	30		58		
Chlorite.....		36	18	33		5-14
Serpentine.....		43		44		8-13
Talc.....		32		63		3-7

In many deposits in carbonate rocks, the talc formed during a final, hydrothermal stage of metamorphism, as a replacement of silicates, especially tremolite, forsterite, and diopside, formed during an earlier stage of higher-grade metamorphism. Thus, wet siliceous dolomites, or dolomite plus introduced silica-bearing waters, have reacted during metamorphism to produce tremolite, with calcite and carbon dioxide released as a by-product.³ Increasing stages of metamorphism at higher temperatures may be characterized by the formation of anhydrous silicates such as forsterite, or more commonly diopside. With later retrograde metamorphism and falling temperatures, these minerals become less stable, and if abundant hydrothermal solutions and magnesia are available, talc and serpentine commonly form at the expense of the earlier silicates.^{4,14}

Examples of deposits of commercial talc derived from crystalline schists and rocks other than ultrabasics or carbonate sedimentary rocks

are recorded in the literature.⁵⁴ These deposits have not been studied in detail, and the evidence for their origin is not clear. Where magnesia and silica-bearing solutions were especially active, however, talc and serpentine are known to have formed as replacements of a wide variety of minerals and rocks. At Natural Bridge, New York, hundreds of cubic yards of granite, syenite, quartzite, and amphibolite along a fault zone have been drenched by such solutions, and largely replaced by talc and serpentine. Some of this talc is of commercial quality. Somewhat similar processes seem to have operated during the formation of some steatite deposits in California.⁴⁶

No supergene talc deposits of commercial importance are definitely known and it seems doubtful that appreciable quantities of talc have formed by supergene alteration of magnesium-bearing silicates and other minerals. Some features of the Johnny Gulch talc deposit in Madison County, Montana, suggest a supergene origin, however. These deposits produced steatite and lava talc during the second World War.⁶⁰

Especially productive and high-grade talc deposits, formed by the alteration of magnesian carbonate sedimentary rocks, occur in northern New York and in California. Other productive talc deposits are found in metamorphosed dolomitic limestones in Georgia, North Carolina, Nevada, and Montana. An important domestic source of talc and soapstone also is from deposits formed by hydrothermal replacement of peridotites, pyroxenites, dunites, and related igneous rocks in Vermont, Massachusetts, and southward along the piedmont in Pennsylvania, Maryland, Virginia, North Carolina, and Georgia.

The New York state talc deposits of commercial importance are in St. Lawrence and Lewis Counties, in the northwest Adirondack Mountains. All of the deposits are of pre-Cambrian age and occur within the highly deformed and recrystallized marble of the Grenville series. The deposits in St. Lawrence County near Gouverneur are by far the largest and most important. In this district, most of the rock mined is a "fibrous talc" composed largely of tremolite, anthophyllite, serpentine, and talc. These and other metamorphic silicates, with quartz and carbonates, occur in elongate, schistose belts interlayered within a northeast-trending belt of siliceous and silicated marble. The "talc" belts have a composite strike length of more than 5 miles and a known continuity down-dip to the northwest in excess of 1500 ft. Movable zones range in width from several feet to about 200 ft (Fig 2). Some of these zones are largely tremolite with less than 20 pct talc, serpentine, and associated minerals. The tremolite was formed largely during advanced stages of dynamothermal metamorphism of the marble in an environment of considerable stress, and much of the talc and serpentine developed during the final stages as fibrous, foliated, and massive aggregates replacing tremolite and anthophyllite.

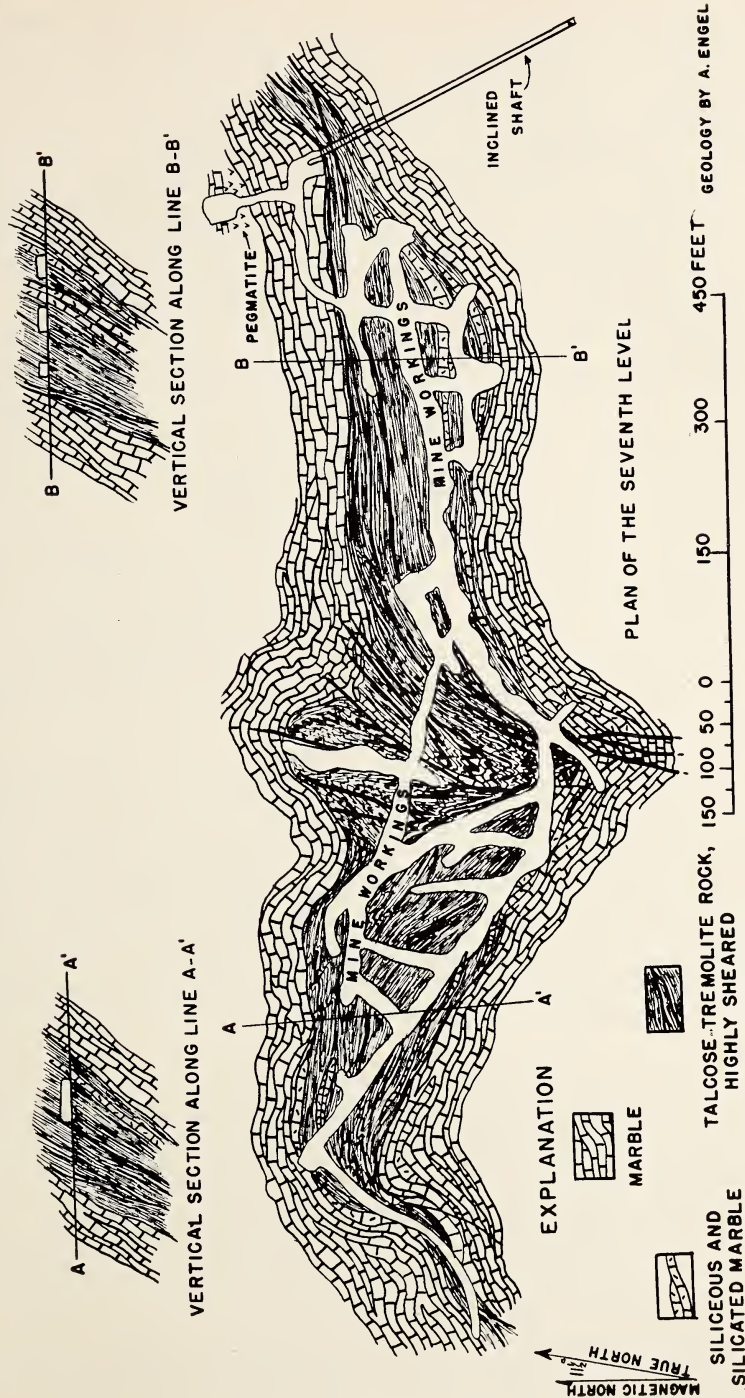


FIG 2—SUBSURFACE MAP AND SECTIONS OF PART OF TALC MINE, TALCVILLE, NEW YORK.

The material mined in Lewis County, New York, occurs about $1\frac{1}{2}$ miles northeast of the village of Natural Bridge. There, an irregular pluglike mass of marble and silicated marble, locally dolomitic, has been highly brecciated and subsequently replaced in part by veins of serpentine, talc, scattered chlorite, prehnite, and quartz. These minerals, with nests of other silicates, especially diopside, and with the carbonates, calcite and dolomite, comprise the commercial talc. Commonly massive serpentine is much more abundant than talc and other minerals. The layered schistose belts of tremolite developed along shear zones in the Gouverneur district, New York, are lacking.

The more productive deposits in California lie in a narrow belt some 200 miles long in eastern California, which extends into western Nevada.⁶⁴ This belt is divisible into three areas, each containing a somewhat characteristic type of deposit, although all have in common an origin through metamorphism and hydrothermal replacement of siliceous and silicated magnesian marbles and limestones.

One area, comprising the southern part of the belt, is east and north of Silver Lake, in San Bernardino County. In this area, the deposits are largely medium-grained tremolite schist, in part altered to serpentine and the mineral talc. These deposits are sheared and reconstituted zones within pre-Cambrian marbles that have been widely invaded by granitic and more mafic igneous material. All talc-forming process occurred during the pre-Cambrian.

A second area is north of the first, in the region of southern Death Valley and the Kingston Mountains. The talc deposits in this area are composed of fine-grained tremolite and siliceous tremolite and of the mineral talc in both foliated and massive varieties. These deposits are also of pre-Cambrian age, although possibly much younger than those near Silver Lake. A very striking feature of the deposits is their localization immediately above and locally below diabase sills that consistently have intruded a lowermost carbonate zone of a metasedimentary series. These relationships pertain in a series of rather widely separated deposits.*

Talc deposits of steatite and near-steatite grade occur in a third area in the Inyo Mountains of California, especially near Darwin, in the southern part of the range.⁴⁶ The steatite talc occurs as highly irregular masses, commonly within dolomitized limestone and silica rock (Fig 3). Both dolomite and silica rocks are of irregular form and distribution. They appear to be of replacement origin. Talc, in turn, has replaced the dolomite and quartz, especially along lithologic contacts and fracture zones. The dolomitization and silicification and the

* The writer is indebted to Mr. Lauren Wright, Associate Geologist, California Division of Mines, for information pertaining to these deposits and for guidance in trips to them.

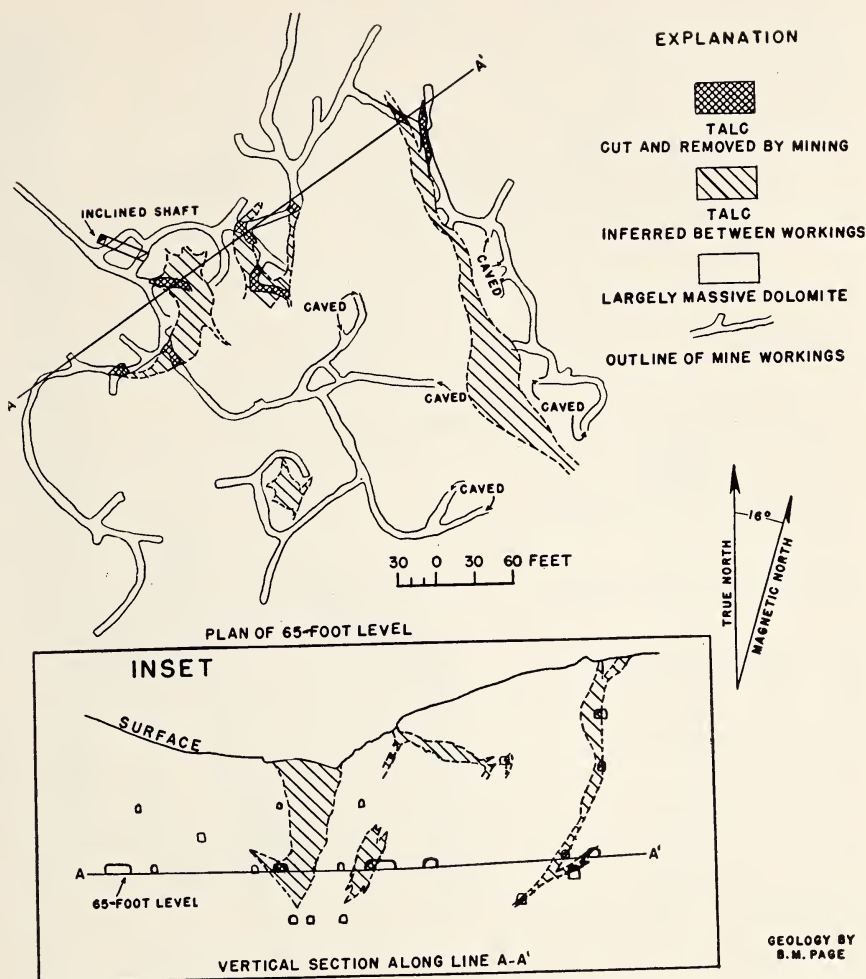


FIG 3—SUBSURFACE MAP AND SECTION OF PART OF TALC MINE, DARWIN, CALIFORNIA.

subsequent steatization have been effected presumably by solutions derived from intrusive granitic rocks emplaced near the deposits.

Two talc districts of the southeastern United States, in North Carolina, and Georgia, also occur along belts of metamorphosed carbonate rocks. In one of these districts,⁵³ talcose zones of Murphy marble (Lower Cambrian) are mined from a belt extending from near Asheville, North Carolina, southeastward through Hewitt in Swain County and Murphy in Cherokee County, across the Georgia line through Fannin County to Ellijay, Gilmer County. A second district is in Murray County, Georgia, where lenticular zones of what are possibly dolomitic schist of pre-Cambrian age, named the Cohutta schist by Furcron and Teague,

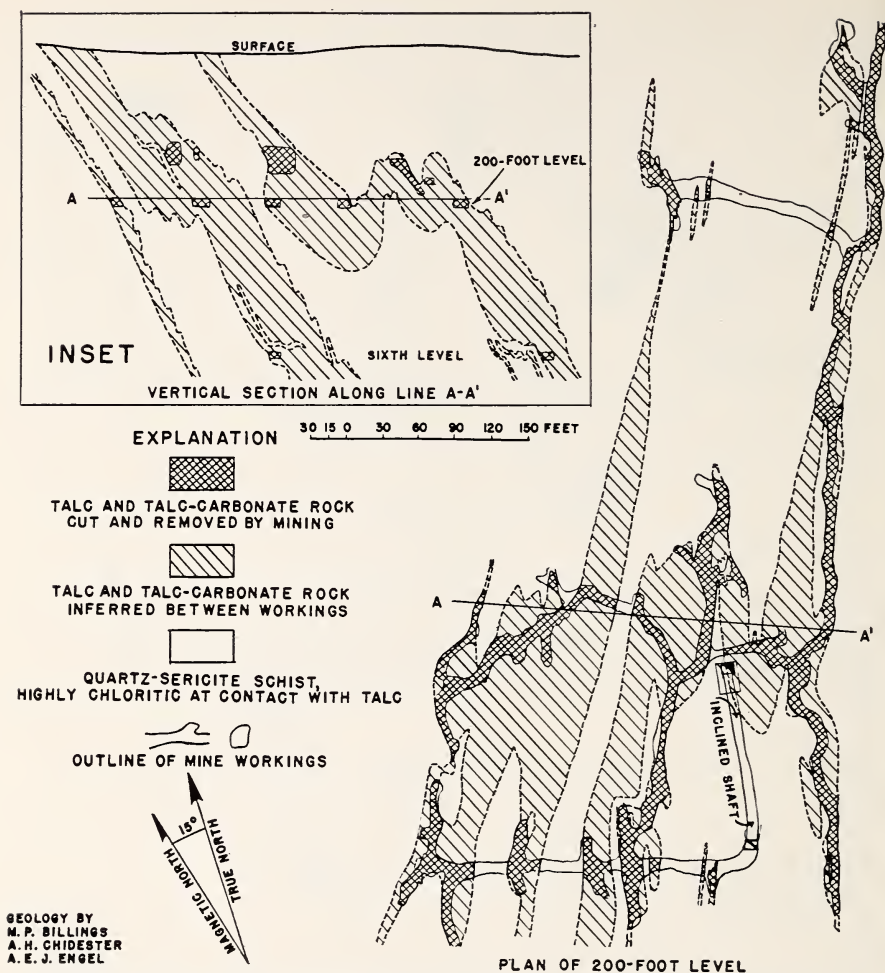


FIG 4—SUBSURFACE MAP AND SECTION OF PART OF TALC MINE, JOHNSON, VERMONT.

have been highly faulted and altered to chlorite, serpentine, and talc-carbonate rocks.¹⁹

The talc and ground soapstone deposits of Vermont are scattered chiefly along the east side of the Green Mountains, from the north-central part of the state southward almost to the Massachusetts line.³² The bulk of the large production from Vermont in the period 1937–1947, however, has come from two deposits in north-central Vermont, one near the village of Johnson (Fig 4), the other about 2 miles southeast of Waterbury village.

Probably all the talc of Vermont has formed as replacement of ultrabasic rocks that were intruded into metasedimentary gneisses, schists, greenstones, and phyllites of the eastern slopes of the Green

Mountains. The intrusives have the form of discontinuous sheets, lenses and pods, essentially conformable with the prominent foliation of the enclosing metasedimentary rocks. Most of these masses were deformed during or after intrusion. The major talc deposits occur where much or all of the intrusive mass was replaced by serpentine, actinolite, talc, chlorite, and carbonates (Fig 4). Most of the serpentine cannot be milled as a talc product. As Hess³⁰ noted, the formation of serpentine has preceded that of talc where the two minerals occur together. The talc, some of it accompanied by as much as 50 pct carbonates, 1 pct sulphides, as well as chlorite, actinolite, and scattered serpentine, occurs generally as lenticular masses (called grit), that in places partly or wholly envelope a relict core of serpentine or, rarely, original ultrabasic rock.

In the larger deposits, as at Johnson, Vermont, the relict masses of serpentine are relatively small and local in occurrence. At other mines such as that near Waterbury, Vermont, the talcose zones form a relatively thin envelope around a prominent central core of serpentine, some of which is verde antique. Metasedimentary wall rocks enclosing the talc deposits and included in it are highly chloritized for distances of several or more feet away from the talc, to form the so-called "blackwall."

Talc deposits somewhat similarly derived^{6,29,30} from ultrabasic rocks occur in Massachusetts and southward along the Appalachians in Rhode Island, Pennsylvania, Maryland, Delaware, Virginia, and North Carolina, and in the northwest United States in Washington.⁶² Of these, only the deposits in Maryland and Virginia have been the source of appreciable tonnages of talc and ground soapstone in recent years. The deposits of Maryland are near Dublin, in Hartford County, and in Carroll, Cecil, and Montgomery Counties. The deposits of Virginia that are of special note are in Nelson, Albemarle, and Orange Counties. Schuyler, in Nelson County, is the center of the principal mining operations.⁶

The more productive deposits of talc outside the United States occur in China (especially Manchuria), India, France, Italy, Norway, and Canada.^{10,49,50,54} In each of about a dozen other countries, however, 1000 tons or more of industrial talc and ground soapstone has been produced in one or more years between 1937 and 1947. These include Australia, Austria, Egypt, Finland, Germany, Greece, Morocco, Rumania, Spain, and Sweden. Reports of occurrences of talc in Russia are rare in the literature.

Some of the Chinese deposits are apparently quite large⁴⁴ and include types of talc formed by the alteration of both magnesian carbonate sedimentary rocks and ultrabasic rocks. High-quality talcs are mined from deposits in Manchuria that are replacements of dolomites in the

Newchwang, Tashichiao, and Haicheng districts in Fengtien. In China proper, the more productive talc deposits are in Chekiang, Fukien, and Shantung Provinces.

European talc deposits of particular note include large deposits on the north slopes of the Pyrenees, in Ariege, France;⁵⁴ in the Cottian Alps west of Pinerolo, Italy; in the Styrian Alps of Austria; and at Vaga, Framfjord, Altermark, and north and east of Bergen, in Norway.⁵⁴ The high-quality French and Italian deposits and apparently the talcs of the Mautern and Rabenwald districts, Austria, are replacements of dolomites and dolomitic limestones. The Norwegian deposits are of lower grade, largely formed by steatization of serpentinite.

Deposits presumably similar to those of the Mautern and Rabenwald districts, Austria, are reported⁴⁹ to exist in the Carpathian Mountains of Czechoslovakia. Talc and ground soapstone have been mined with block talc at Zoptau and Wernsdorf, Moravia, as well as in Sweden, near Handoel in Jaemtland, in Greece, and in the Fichtelgebirge, Bavaria. The deposits near Wunsiedel, from which much of the German production has come, formed largely by reaction and alteration of dolomite, quartz, and calcium and magnesium silicates.^{10,54}

Most of the Canadian talc production^{49,63} comes from deposits near Madoc, Hastings County, Ontario, less than 100 miles northwest of the Gouverneur district, New York. At Madoc, talc with some serpentinite replaces recrystallized layers of dolomite in the marble of the Grenville series. Wilson⁶³ concluded that the talc formed largely as a result of permeation of dolomite by siliceous hydrothermal solutions. Nests and layers of tremolite and other metamorphic silicates occur only locally.

In India, the more productive talc deposits occur in Jaipur State, in Rajputana, although production of talc is recorded from deposits in the Jubbulpore district in the central provinces, Hazaribagh in Bihar, Salem and Mellore districts in Madras, at Hamirpur, in the United Provinces, and in Mysore.

PRODUCTION AND CONSUMPTION

The United States is by far the largest producer of talc and ground soapstone, accounting for roughly one third of the world production in 1946.⁵⁹ In 10 years, the domestic production has almost doubled, from about 216,000 short tons valued at \$2,252,629 in 1936 to some 419,000 short tons valued at \$5,869,109 (at shipping point) in 1946. Throughout this period, New York remained the largest producing state, with an annual output averaging more than 100,000 tons. California and Vermont, producing, respectively, about 78,000 and 75,000 tons in 1946, are the next largest producers, with remarkably parallel and increasing tonnages through the period 1936-1946. Total value of California talc produced annually is much greater, however, than that produced in Vermont.⁵⁹ Most of the remaining talc output in the United States comes

from Georgia (over 36,000 tons in 1946) and Maryland, which has produced between 15,000 and 20,000 tons annually in recent years. In 1946, Virginia, Pennsylvania, Montana, Texas, Washington, North Carolina, and Nevada also produced some talc or ground soapstone.⁵⁹

About three fourths of the talc produced in the United States is consumed in five industries—paint, rubber, roofing, ceramics, and insecticides; the paint industry consuming about one fourth of the total.

Foreign talc production apparently has varied greatly during recent years, although production figures are not available for many countries. China, Italy, France, Korea, Canada, Austria, and India accounted for the bulk of the foreign output of roughly 800,000 tons in 1946.

In 1946, foreign imports of talc and ground soapstone into the United States totaled about 18,400 short tons valued at \$394,881.⁵⁹ Almost all this talc came from three countries: Italy (10,665 tons valued at \$283,379), Canada (5787 tons valued at \$63,911), and France (1241 tons valued at \$26,656). This importation in 1946 is in marked contrast to that during 1940, when France, China, and India contributed almost 14,000 short tons of approximately 29,000 tons imported.

PROSPECTING AND EXPLORATION

Surface exposures of talc at many of the large talc-producing districts in the United States attracted the attention and active interest of Indians and early white settlers. Exploration of these deposits with a view toward mining, however, was not begun in the larger eastern districts until the last quarter of the nineteenth century. Many deposits of California remained unexplored until 1915.

Before 1930, exploration for talc beyond the surface inspection and sampling of outcrops almost invariably became a function of mining. Thus, masses of the desired rock were quarried or more commonly traced downward and laterally by shafts, adits, and drifts. These workings were enlarged into rooms, glory holes, and stopes wherever the extent of the commercial-grade rock seemed to warrant.

Few workings or drill holes were driven intentionally beyond the limits of desirable rock to determine more about the size, form, and distribution of the known deposit or to find new deposits. Mining operations usually were on a small scale and had limited financial backing, so most of the rock removed in any mine was destined for the mill.

Many data of value in prospecting and exploration for new talc deposits within many parts of the United States have been obtained through geological studies, especially of the federal and state geological surveys. Detailed geologic maps and reports of the larger talc districts of New York, Vermont, California, and Georgia have been published or will be issued shortly.^{14,19,46,64}

Core drilling is now used extensively in the search for talc, especially

within or near some large producing mines and districts. In recent years, as much as 7000 ft of core has been drilled annually by several talc companies in the Gouverneur district, New York. Of this footage, about half was surface drilling in search of deposits inferred from geological considerations to lie beneath a surface cover of alluvium and glacial drift. In some parts of this district, the close association of lead and zinc minerals with talc bodies has resulted in the discovery of commercial talc deposits in conjunction with the development of metal mines. In the same way, the search for and mining of talc has revealed a previously unknown deposit of lead and zinc. In Vermont, the close association of talc with verde antique and asbestos has been of similar reciprocal value in the discovery and exploration of these deposits.

TALC MINING

In general, methods used in mining talc are less progressive than those used in most metal mines. Numerous natural obstacles in the way of efficient operations are presented by complexities of form, structure, and composition of many talc deposits. The introduction of good equipment and modern mining methods by capable operators is becoming increasingly evident in most large districts, however, and some projected plans of large companies, if effected, will result in a more ideal exploitation of the talc deposits.

At present, most of the industrial talc and ground soapstone is mined underground, although a small amount is obtained during surface quarrying of block talc, which is described in the chapter on Dimension Stone.

Many talc deposits have a moderate to steep dip or plunge and it is common practice to sink a shaft in the talc on the footwall side of the desired rock. Since the commercial talc is traced downward by the shaft, changes in dip or plunge of the talc body are reflected in corresponding irregularities of the shafts.

Straight inclined shafts have been sunk recently to mine talc deposits in Vermont, New York, and California. A vertical shaft is employed in mining the talc deposit at Madoc, Ontario, and another is being sunk to mine a talc body at Balmat, New York.

Adits are employed in areas of appropriate relief, as at the large talc mine southeast of Waterbury, Vermont, and in mines in Murray County, Georgia, and San Bernardino and Inyo Counties, California. Most of these adits are being replaced by shafts as the deposits are followed downward.

In most talc mines, drifts and crosscuts driven from shafts are used to explore and outline the body of minable rock, as well as for tramways and subsequent mining needs (Figs 2, 3, 4). Since many deposits are of irregular, folded and faulted forms, the drifts are very crooked.

Considering the sheared, incompetent nature of many talc bodies, the amount of timbering done is small. Notable exceptions are the main (adit) level of the mine near Waterbury, Vermont, and several mines in the southern Death Valley-Kingston range, California, which are timbered throughout most of their length.

It is common practice in mining the talc bodies to drive raises at frequent intervals, often 30 to 50 ft, in whatever minable talc is encountered, as far as the overlying levels or as far as safety or the upper limit of the talc permit. These raises are then enlarged, the broken rock falling to the drift floor to be mucked by hand or mechanically. A

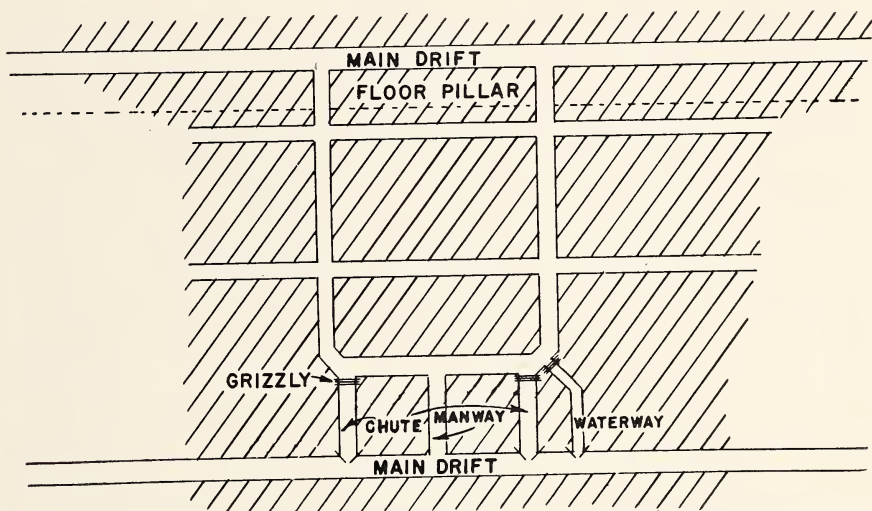


FIG 5—SCHEMATIC DIAGRAM SHOWING METHOD OF MINING AN INCLINED, RUDELY SHEET-LIKE OR LENTICULAR TALC BODY BY SUBLEVEL STOPES.
Section is drawn in the plane of the talc zone.

few large old stopes or glory holes in California and Vermont talc mines are subject to frequent cavings and thus tend to "work themselves." In the soft talcs of the Monarch mine, Kingston Range, California, each stope must be timbered as the talc is removed, to prevent collapse of the openings.

Recent practice in many talc mines tends toward the development of conventional sublevel stopes wherever possible, with grizzlies and chutes (Fig 5). A valuable addition is a waterway with a fine-spaced grizzly placed at the intersection of appropriate raises and sublevels (Fig 5) to drain off water that otherwise would soak the muck and impede milling. Excess water is no problem in the California mines, which are, in fact, too dry. Commonly sufficient water for operations must be hauled many miles.

The underhand stoping (benching) method of mining is employed

where possible. In the talc mine at Johnson, Vermont, and locally in the Gouverneur district, New York, blocks of ore are mined by long-hole drilling. Shrinkage stoping has been used at Madoc, Ontario, but is not a common practice in talc mining, partly because of the capital tied up in the operation and partly because muck lying for long periods in stopes may become discolored, excessively wet, or contaminated.

In most districts, the drilling of headings is done either with stopers or jackhammers mounted on jack legs. In the soft talcs of California, some raises and stopes are opened with spade and bit points mounted

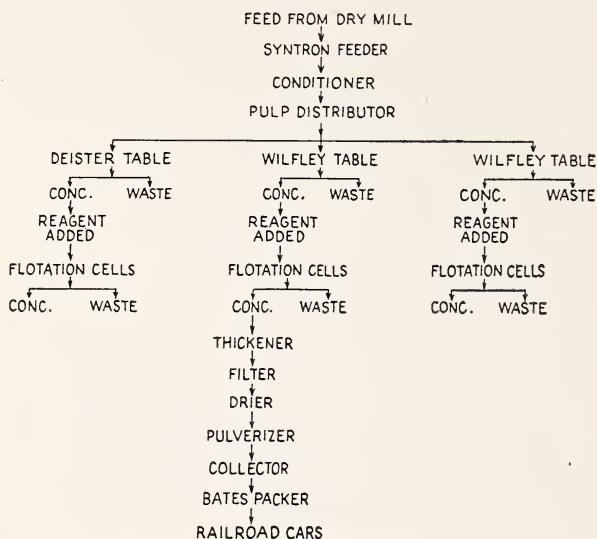


FIG 6—FLOWSHEET OF FLOTATION PLANT IN TALC MILL, JOHNSON, VERMONT.

on jackhammers. Wet drilling is employed exclusively in the New York mines to reduce the hazard of silicosis and fibrosis.^{9,48}

Conventional practice in the large talc mines involves the use of air and electrically operated mucking machines such as rocker shovels, for mucking crosscuts and drifts. Small battery locomotives are rapidly replacing hand tramming in large talc mines. In New York and California, some companies sort talc at the mines according to color and impurities, either underground or on wood and steel plates at the headhouse. Under the plates is a series of bins into which the sorted talc is dumped pending its removal to the mills.

PREPARATION FOR MARKET

Talc milling³⁹ is largely a grinding operation accompanied by air separation. Most of the industrial talcs are dry-ground. Some talc is further beneficiated by wet flotation¹⁷ at Johnson, Vermont (Fig 6). Experiments have been conducted in the flotation of talcs from New York⁴⁵ and elsewhere,²⁴ also. Driers are commonly employed where much wet

talc is mined, as in New York and Vermont, since the wet material reduces mill capacity as much as 30 pct. In general, talc mills are close to mines except in California, where much of the talc must be hauled 100 miles or more.

Most industrial talcs are ground to one of three very general size groups: 96 pct minus 200-mesh screen; 98.5 pct minus 325-mesh; and 99.5 pct minus 325-mesh. Actually, in achieving these specifications, much talc may be "overground," with a resulting large spread in particle dimensions. Many fines, 15 to 35 microns in size, commonly result.

Extremely fine grinding with so-called micronizers and fluid-energy mills is done in certain New York and Vermont mills. Standard particle sizes, ranging principally between 0.5 and 25.0 microns measured by air-permeation methods, are attained. The micronized talc is employed in paint and paper industries.

Conventionally, in talc milling, rock taken from the mines is crushed in primary and then in secondary crushers to $\frac{1}{2}$, $\frac{5}{16}$, $\frac{3}{8}$ or $\frac{1}{8}$ -in. products. Fine grinding is achieved in tube mills, Raymond mills, and Hardinge mills, in closed circuits with Sturtevant, Raymond, or other types of air separators. The ground material is bagged by hand in a few mills; more generally, by semiautomatic packers such as the Hawes packer, or automatic Bates valve packers, in 50, 75, 100, or 200-lb sacks for shipping.

The following milling procedure is contemplated for a new mill in the Gouverneur district, New York:

Primary crushing with gyratory crusher at the shaft headhouse

Conveyor to plant 500 ft away

Wet-ore storage

Drying of minus $\frac{3}{8}$ -in. product

Secondary crushing with Symons shorthead cone in closed circuit with $\frac{1}{8}$ -in. screen

Dry-ore storage

Weightometer

Extremely fine grinding with C. H. Wheeler Company air mills and standard grinding with Hardinge mill in closed circuit with Raymond separator

Fuller-Kinyon conveying to bulk-storage bins to packing house

Bates valve packers

Power and gravity conveyors to cars

MARKETING, USES, TESTS, AND SPECIFICATIONS

Talcs have a wide variety of uses and markets, for which tests and specifications of grain size, shape, color, chemical and mineral composition, weight per unit volume, oil absorption, and hardness are employed.

The paint industry is by far the largest user of talcs. In addition, each of the following industries uses more than 10,000 tons of talc and ground soapstone annually: roofing, ceramics, paper, rubber, cosmetics, textiles, and insecticides.

Uses in Paints

The paint industry uses more than 75,000 tons of talc annually. In general, high grades of white talc are employed, most of which is the fibrous variety typified by that mined near Gouverneur, New York; although flaky and more massive talcs also are used. The fibrous talcs consist largely of tremolite, anthophyllite, serpentine, and talc in various proportions. The nonfibrous talcs commonly contain some serpentine or carbonates in addition to talc.

Talc is used in paint as an extender and, especially in the cold-water paints, as a pigment. Color, particle shape and size, packing index and oil absorption are considered in specifications of paint talcs. The fibrous talcs presumably serve as locking or bonding agents in the paint film, and the more shredlike or flaky talcs seem to act as a laminal pigment.^{18,20} Fibrous particles also seem to hold up heavier pigments and thus prevent settling and caking of shelf goods. The extreme whiteness of talcs, especially the better grades mined in New York and California, offers excellent hiding power.

A relatively fine particle size—98.5 to 99.5 pct through a 325-mesh screen—is commonly desired for paints. Milling of talc to particle sizes as low as 0.5 micron is also employed in preparation of some talc for paints.

A conventional standard for classifying talcs prepared for paints is an oil-absorption test such as the Gardner-Coleman test.²¹ In general, fine grinding increases the quantity of a given oil required to wet thoroughly all the absolute particle surface of the talc. For a given particle size, industrial talcs composed entirely of the mineral talc have a higher oil absorption than talcs high in tremolite, quartz, or carbonates. Highly fibrous or flaky grains have greater oil absorption than nearly equant grains. Common industrial talcs range from about 30 to 60 in the scale of oil absorption; much talc tests between 30 and 45. A packing index may also be used as an indicator of particle shape and weight per unit volume.

Pronounced variations in the chemical and mineral composition of talcs employed in paints are common and permissible. Minerals that grind to colors other than white, and sulphates such as gypsum and anhydrite, are quite objectionable, however.

Uses in the Ceramic Industry

The use of talcs in the ceramic industry^{5,36,37} is increasing greatly, inasmuch as they impart highly desirable properties to ceramic products.^{5,8,56} Large tonnages of talc are used in the preparation of white-ware bodies,^{22,28} including semivitreous tableware, electrical porcelain, high-frequency insulation,^{23,58,56,57} and glazed wall tile.³⁶ Talc is used

also as an important ingredient of sagger bodies⁸ and other kiln furniture.²

Ground talcs of steatite grades are being used on an increasing scale as synthetic lava talc to supplement and replace natural block talcs,¹³ which are of limited occurrence and costly to mine and machine.⁴⁹ Thus many electrical, chemical, and refractory articles are made by dry-pressing or extruding and firing powdered steatite, which may be compounded with a binder and fluxes.⁵⁸ Talc composes as much as 80 pct or more of these mixtures.

The value of talc to the ceramic industry includes^{37,42} its high specific heat, resistance to acids, content of magnesia that acts as a flux, and low shrinkage under heat-treatment. Talc also imparts to the ceramic body a high resistance to thermal shock and in whiteware bodies some types of talc seem to prevent delayed crazing.²⁷

In general, a wide commercial acceptance of talcs for ceramics is contingent upon adequate sources of material of uniform chemical composition and physical properties that will ensure constancy in shrinkage and in other properties when the ceramic body is fired.^{49,52,61} This need for uniformity over long periods of time in the talc employed imposes severe demands on the miner and miller.

Specifications are also placed upon the proportions of various components. In the steatite-grade talcs, which are used in the manufacture of high-frequency insulators, more than 1.5 pct CaO, 1.5 pct iron oxides, and 4 pct alumina are objectionable.³⁸ In certain whiteware bodies, however, a CaO content of as much as 6.5 pct is not objectionable; in fact, it may be desirable.²⁸ In general, the presence of manganese and iron is undesirable because they cause discoloration in fired ceramic bodies.³⁸

Talcs used in many ceramic bodies commonly are ground to pass through a 200-mesh screen. Grinding to finer particle size is common but is not always necessary for many tile and other ceramic bodies.⁶¹

Roofing Industry

The roofing industry ranks about second in recent years as a consumer of talc, employing from 11 to 15 pct of the total consumption. Lower grades of off-color and impure talc are usable, and this market, with the insecticide industry, serves as the principal consumer of low-grade talcs. The talc acts to some extent as a filler, especially as a non-sticking, inert, fireproof, and weather-resistant surfacing on tar paper, asphalt shingles, and roll roofing.

Uses in Cosmetics

The cosmetic trade uses some 20,000 tons or more of talc annually in soaps, creams, salves, rouges, toilet powders, and other toilet preparations. Much French, Italian, and Chinese talc has been and is used for

this purpose but the amounts of domestic talcs so employed are increasing. This market, however, is important to only a few domestic producers. Talcs used in cosmetics necessarily must be free of grit, of excellent color, and of small particle size.

Uses as a Filler

Talc is widely used as a filler and dusting agent, especially in the rubber and insecticide industries, where the lower grades of off-color talc and ground soapstone are employed. Talc is also used as a filler in putty, wall plasters, composition floorings, linoleum, oilcloth, rope, string, cordage, textile fabrics, and elsewhere.³⁹ Talc is a dusting agent in the manufacture of wire nails, linoleum, oilcloth, leather, corks, glass, candy, and chewing gum.

Miscellaneous Uses

The softness and high slip of some talcs make them valuable as lubricants in some cup greases and in dies. Talc is employed to polish nails, glass, and cereals, especially rice, barley, and corn. It is used as an absorbent in some explosives, in drying oily leathers, and other oily surfaces. Small amounts of talc are used as bleaching agents, to absorb odors from foods, to dust wounds and sores of animals, to filter water, in stove and auto polishes, in floor wax, and in sundry other ways.³⁹

PRICE HISTORY

All grades of talc have increased in price in the 10-year period between 1938 and 1948, as has the average value of ground talc. These increases and other related data on production for the years 1937 and 1946 (most recent figures available at this writing) are shown in Table 3.

In addition, the quoted prices of domestic talcs have continued to increase somewhat between 1946 and 1948. Thus, New York talcs as of November 1948 are quoted as follows: 98 to 98.5 pct minus 200-mesh, \$22 to \$22.50 per ton; 98 to 99.5 pct minus 325-mesh, \$23 per ton; and talc ground to 7 to 8-micron average particle size (as measured by air-permeation methods), \$35 per ton. Somewhat comparable increases in prices of talcs from other districts, during the period 1946 to 1948, are reported.

The higher priced talcs from California, which sold for as much as \$40 in 1946 and \$42.75 in November 1948, are largely of steatite grade. Neither the New York nor Vermont deposits contain steatite. None of the California talcs are ground to sizes below 99.5 pct minus 325-mesh at present, although fine grinding of these talcs is contemplated in the future.

Extremely fine grinding necessarily increases the cost per ton of talc to industrial consumers, but if appropriate methods are used, net costs are lower when the fine grinding remains an integrated phase of the

TABLE 3—Prices, Grades, Tonnages, and Values of Some Domestic and Imported Talcs in 1938 and 1946

Year	Sources	Grades	Price Range	Short Tons	Average Value per Ton	Total Value
1938	California	98 pct minus 200-mesh to 99.5 pct minus 325-mesh	\$10-\$30	30,059	\$12.69	\$ 391,456
1938	New York	96 to 99.5 pct minus 325-mesh	\$10-\$18	86,423	\$12.89	\$1,110,024
1938	Vermont	98 pct minus 200 to 99.5 pct minus 325-mesh	\$ 8-\$16	35,126	\$ 9.37	\$ 329,084
1938	Entire U. S.	All grades		192,775	\$10.45	\$1,936,532
1938	Foreign imports ex dock	All grades steatites and cosmetic talcs abundant	\$10-\$85	22,127	\$17.67	\$ 391,198
1946	California	98 pct minus 200 to 95.5 pct minus 325-mesh	\$17-\$40	78,170	\$18.35	\$1,434,978
1946	New York	96 to 99.5 pct minus 325-mesh	\$13-\$21	112,000	\$18.86	\$2,112,250
1946	Vermont	98 pct minus 200 to small amounts of micronized talc	\$10-\$22	75,144	\$11.22	\$ 843,247
1946	Entire U. S.	All grades		407,150	\$13.84	\$5,635,267
1946	Foreign imports ex dock		\$10-\$100	18,415	\$21.41	\$ 394,411

initial milling of talc, rather than when it is attempted as an independent secondary process instituted by an industrial consumer. Accordingly, the trend is toward finer grinding by producers of some talcs, which are used especially in the paint industry.

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CHAPTER 49

TITANIUM

By JOSEPH L. GILLSON*

TITANIUM is one of the most abundant elements in the minerals that make up the earth's crust but its use in industry is only a generation old; yet probably no other important commercial mineral raw material (except possibly magnesium) has undergone more changes and developments in sources of supply, in processing techniques, in uses and applications, in the past 10 years, or stands on such a threshold of still more advances. Its outstanding use today is as the oxide, and because of its extreme whiteness, high refractive index, chemical stability, and relative cheapness, it has become the white pigment used in the largest volume. New developments in the uses of titanium metal, potential and actual, may surpass the pigment use of the oxide before many years.

TITANIUM-BEARING MINERALS

Although a number of minerals contain titanium as the principal metal, only a few are of commercial importance. These are arizonite, ilmenite, and rutile. The other oxides, brookite, pseudobrookite, and anatase, occur in a few deposits, one at least of minor importance. The silicate titanite, and the double oxide of calcium and titanium, perovskite, occur in a few deposits in quantities sufficient to be considered as potential ores were not richer deposits of the oxides available elsewhere.

Arizonite is a name given by Palmer^{16a} to a mineral found some years ago in minute quantities in Arizona, which has the formula $\text{Fe}_2\text{O}_3 \cdot 3\text{TiO}_2$. Unexpectedly, it was found that the black titaniferous iron oxide found in large quantities on the beaches of many continental land masses corresponds in chemical composition to this formula (although ferrous oxide is always present). No one has yet been able to prove that the commercial mineral on the beaches is truly arizonite, or an allotropic modification of it, since X-ray investigations by Howard Carl and A. F. Gabriel, of the U. S. Bureau of Mines, and by the X-ray laboratory of the Chemical Department at the Experimental Station of the du Pont company, have shown only that the sand mineral gives just a jumble of lines, rather than an identifiable pattern. Lack of a better name.

* Geologist, E. I. du Pont de Nemours and Co., Wilmington, Delaware.

and the inability to prove that the mineral of the beaches is not arizonite, favors application of that name to it. In the trade, however, the name arizonite has not yet been accepted, and the mineral is sold as "ilmenite." The two black minerals cannot be distinguished except by chemical analysis or by the examination of polished sections under the metallographic microscope.

Ilmenite, $\text{FeO} \cdot \text{TiO}_2$, occurs in rock deposits and as sands on a few beaches. In rock deposits of the anorthosite type, it occurs intergrown with either hematite or magnetite in massive lenses, in which the crystals are allotriomorphic except in pegmatitic facies. It occurs as disseminated grains in schists, and fairly well-formed tabular crystals have been found in some places in such rocks.

Rutile, one of the three allotropic modifications of the single oxide TiO_2 , is so widespread in nature that it is found in nearly all rocks as an accessory, and in many kinds of rocks it is concentrated sufficiently to make them actual or potential ores. Because the color varies from red to black, even in the same deposit, the identity of some of the mineral grains is difficult to determine visually.

Leucoxene^{12a,29} is a name given to altered ilmenite (or arizonite), and since enough altered grains are present in many commercial ores to affect the overall composition, the mineral (or minerals) so named must be recognized as products of sufficient importance for separate identification. Actual pseudomorphs after ilmenite are found in some rock deposits and these are gray in color. In beach sands, brown as well as gray grains are found, many with a core of unaltered arizonite. When concentrated separately, these altered products analyze from 70 to 92 pct TiO_2 . Since the material is insoluble in acid, it is not acceptable as feed for pigment manufacture by the acid process, but is very desirable for other processes. Probably leucoxene is not a separate mineral species and may be a submicroscopic aggregate of rutile crystals. The brown grains may be different mineralogically from the gray. Both occur in the sand at Trail Ridge, Florida, and can be partially separated magnetically—the gray being the less magnetic—and they are higher in TiO_2 .

CLASSIFICATION OF DEPOSITS

Two large divisions of deposits occur—rock and sand. Until recently, the latter have been the most important commercially, but continued development of some long-known large rock deposits and a recent find of a very large new rock deposit, and metallurgical developments permitting more favorable use of such rock ores, are directing the trend of development toward the rock deposits, so that in time the sand deposits may be of lesser importance.

In turn, both sand and rock deposits can be further subdivided, as follows:

Rock Deposits

Anorthositic Type—The anorthositic type is represented by ilmenite-magnetite and ilmenite-hematite in lenses of massive ore and disseminated as individual grains in rock masses of indefinite shape. Rutile occurs in Virginia disseminated in a feldspathic rock that is probably anorthositic, at least in correlation. In the author's opinion, these deposits are all metasomatic replacement in origin but many experienced geologists believe them to be magmatic segregations.

Schist Type—Both ilmenite and rutile occur disseminated in schists but at no place has any such rock been found in which the concentration has been sufficient to permit economic recovery. However, soils derived from the weathering of such rocks are enriched in the insoluble minerals, and are worked for ilmenite and rutile in a few places. Stream placers resulting from erosion of deep soil zones containing some concentration of these minerals were worked in Brazil and are of considerable importance as a reserve of rutile.

An unusual occurrence of a dike-like intrusive mass of ilmenite in a gneissic rock occurs in North Carolina, which is the unique example of this type. At Kragerö, in southeastern Norway, dikes carrying rutile, apatite, and pyrrhotite occur in schists cut by gabbros.

Miscellaneous Types—An occurrence of rutile concentrated in one of the serpentine masses of upper Maryland⁶³ is also unique in the knowledge of the author.

An occurrence of the four titanium oxides, rutile, anatase, pseudobrookite, and brookite, in a pegmatitic phase of nepheline syenite and in surrounding metamorphosed sediments at Magnet Cove, Arkansas,^{23a,59} is unique in that only there had sufficient concentration of the minerals occurred to permit mining of the rock as an ore. These minerals are found in many alkaline rocks as accessories.

Minor occurrences of rutile in quartz veins and in pegmatites have been reported. An interesting example occurs in the Stillwater Range, Churchill County, Nevada, where rutile is disseminated in a silicified zone in Tertiary intrusives. A large mass of pegmatite near Pluma Hidalgo, in the State of Oaxaca, Mexico, carries considerable ilmenite, which formed in masses of pyroxene that had replaced feldspar. Very locally, rutile had formed where solutions rich in titanium found no iron mineral with which to react.

An occurrence of rutile in silicified volcanic ash in the Medley district in Jeff Davis County, Texas, has been described by Vogel.^{64a}

Sand Deposits

Beaches, dunes, and stream sands in many parts of the world are enriched by gravity segregation in the heavy minerals that are chemi-

cally resistant to weathering and physically hard enough to withstand considerable abrasive action. In addition to titanium minerals, such sands are worked for tin, zircon, rare earth minerals (especially monazite), and, of course, precious metals and diamonds. Zircon occurs in all such placers in varying degrees of abundance and is recovered as an important by-product in many operations for obtaining titanium minerals.

Deposits of arizonite are found only on ocean beaches of continental land masses, for a definite reason that will be explained later. Sand deposits of titaniferous iron ores occur as dune and beach deposits in many volcanic areas, of which that in New Zealand is the outstanding example. Sand deposits of which rutile is the only important titanium mineral occur on the eastern shore of Australia. Ilmenite is the black titanium mineral found in beach sands along the Atlantic Seaboard of the United States, in greater or lesser concentration, from Cape Cod to the mouth of the St. Mary's River in northern Florida. South of there the black mineral in the sands is arizonite. The writer believes, without adequate data to support the conclusion, that arizonite came out of the granites and gneisses of Georgia and Alabama whereas the ilmenite came out of schists of the Piedmont of the Carolinas and middle Atlantic states.

Stream placers are worked for rutile in the Cameroons.

The most important beach deposits in the world are in Travancore, India, from which a large proportion of the ilmenite supplies of the world were produced prior to World War II and since these will continue to be important, they are described in considerable detail in the following pages.

GEOLOGICAL DESCRIPTION OF IMPORTANT DEPOSITS

Rock Deposits

There are so many rock deposits containing titanium that only a few can be described in detail. Those worked commercially to date are the titaniferous magnetite at Sanford Lake,^{5,23} in the central Adirondacks of upper New York state; the big dike of titaniferous magnetite called Storgangen, in southern Norway; deposits of ilmenite-hematite near St. Urbain County, Charlevoix, Quebec; ilmenite-nelsonite and rutile-syenite rocks in Virginia, and the unique ilmenite dike in Caldwell County, North Carolina. The tonnage produced at the first named locality is providing about half of the titanium ores currently consumed in the United States. The Norwegian deposit is the principal source of titanium in western Europe but is supplying some ore to the United States. The productive capacity is to be increased¹⁴ by 50 pct. Tremendous deposits of ilmenite-hematite ore found in eastern Quebec,

north of Havre St. Pierre, on the north shore of the Gulf of St. Lawrence, will be in production in 1951.^{3b}

Titaniferous Magnetites

DEPOSIT AT SANFORD LAKE, ADIRONDACK MOUNTAINS

The Sanford Lake deposit occurs within the central anorthosite core of pre-Cambrian rocks of the Adirondack Mountains. The nontitaniferous iron ores of the Adirondacks, which are all outside of the anorthosite, occur in the so-called Keene gneiss. The anorthosite is named the "Marcy," after the peak of that name, which is the highest mountain in the state and in view from the ilmenite-magnetite mine. A border (?) facies is called the "Whiteface," from the mountain of that name.

So many petrologists who have written on the genesis of the anorthosite have explained the Whiteface as a border facies, have called the associated gabbro masses either earlier inclusions or later pyromagmatic intrusions, and the ore a magmatic segregation,^{45,61} that the author hesitates to disagree with their conclusions, but observation extending over many years has forced him to do so.

The following general statement in regard to the deposits was written for this chapter by B. K. Haffner, former resident geologist of the National Lead Co. at its MacIntyre operation at Sanford Lake:

"The ilmenite-magnetite ore deposits of the Lake Sanford district in Essex County, New York, occur in a large anorthosite body, about 4 miles north of the southern boundary. The anorthosite is typically a very pure coarse-grained feldspathic rock, with the feldspar having a composition corresponding to a basic andesine. Near the major ore bodies, there occurs in places a fine-grained gabbroic phase of the anorthosite which contains a moderate amount of pyroxene, garnet, amphibole, and biotite. In the gabbroic rock, the garnet, amphibole, and biotite are apparently secondary alteration minerals.

"The ilmenite-magnetite ore occurs as roughly tabular masses, as much as 2000 ft long and several hundred feet thick, with dips from 45° to 90°. The ore varies in character between a very massive, pure, coarse-grained mixture of approximately equal amounts of magnetite and ilmenite, with an average grain size of about 5 mm, and a finer-grained disseminated type of ore, which shows gradations from a disseminated gabbroic rock to a nearly pure aggregate of fine-grained magnetite and ilmenite with an average grain size of 1 to 2 mm. The coarse-grained ore occurs as a wide band along the footwall of the ore body, with the finer-grained type of ore lying in bands parallel to it with interspersed bands and lenses of waste rock. At least two major faults are known to cut through the ore, offsetting the ore bands two or three hundred feet. As far as present exploration has shown, the width of the ore body increases with depth.

"A list of minerals found in or associated with the ore includes pyrrhotite, pyrite, and small amounts of the sulphides chalcopyrite, cobaltite, sphalerite, galena, molybdenite, and marcasite. Also occurring with the ore are the carbonates, calcite, siderite, and ankerite; also several varieties of apatite, and tourmaline, scapolite, and prehnite, besides the usual rock minerals and alteration products."

Supplementing this general description, the author has the following opinion on the genesis of the deposits. The Marcy anorthosite, which is an exceedingly coarse-grained rock resulting probably from magmatic intrusion, consists of a plagioclase, the crystals of which began to grow as labradorite but which became somewhat more sodic as the rock solidified. The rock mass, still hot but probably solid, was soaked with solutions and the process generally called "albitization" occurred; but the "albite," characteristic of more acid rocks, was here an andesine, because of the presence in the solutions of sufficient lime. In the writer's opinion, the Whiteface anorthosite is not a "border" facies at all but simply an "andesinized" product of the original Marcy type. It certainly is not confined to the border of the mass but occurs in nearly every acre of surface exposed that the author has examined. As the solutions that caused the andesinization continued to be delivered from some deeply buried residual reservoir, they became richer in other oxides, and eventually in those of iron and titanium. A metasomatic "gabbro" formed, of which the most conspicuous dark-colored mineral is garnet, and the texture of the rock is not that typical of pyromagmatic masses but the grains are allotriomorphic. Convincing evidence of the metasomatic origin of the gabbro is that residual crystals, some of large size, of the big labradorite "phenocrysts" of the Marcy anorthosite are found in it. All have reaction rims around their edges and many are "invaded" or bisected by stringers or veinlets of andesine, with garnet, hornblende, hypersthene, etc. Although never previously mentioned in descriptions of the "gabbro," such residual grains of labradorite "phenocrysts" are not rare; they can be found by a little search in every block blasted out of "gabbro" zones found lying on quarry benches, and they can be seen along quarry faces. Furthermore, original gneissic structures that appear here and there in the anorthosite are preserved in the "gabbro," although the individual mineral grains are even-granular and uncrushed. Apatite and scapolite are widespread accessories, and these are typical metasomatic minerals—the former in other titaniferous ores of that genesis;^{43,55} the latter in contact-metamorphic zones.

The ore is a replacement of both anorthosite and "gabbro"—the replacement of the coarse-grained feldspathic rock made a coarse-grained ore generally low in iron silicates (and hence easily concentrated), whereas the gabbroic ore is fine grained, rich in iron silicates, especially garnet and hornblende—both of which tend to go along

with the ilmenite into the final concentrate. For some reason or other, not readily apparent, some of the gabbroic ore is higher in TiO_2 than the anorthositic ore.

The ilmenite grains are free from magnetite inclusions but the magnetite grains contain "clouds" of microscopic crystals of ilmenite, which cannot be separated by ore-dressing methods.

Since the preparation of this manuscript, some new conceptions of the formation of titaniferous magnetite deposits have been advanced. Ramberg^{49a} suggests that these deposits are recrystallizations under dynamic metamorphism—the titanium and iron were liberated when hornblende and biotite were changed into new minerals and when sphene was absorbed in lime silicates. He believes that the elements so liberated migrated moderate distances and crystallized as ilmenite and magnetite, and as intergrowths of the two. Sullivan^{62a} considers titanium as a lithophile element, and relates it to crystallization by "granitization," and does not connect it with magmatic stoping, a conception in keeping with the ideas of the writer expressed above. Evrard^{17a} has evolved a complex physical-chemical interpretation for explaining crystallization of titaniferous ores from a magma, considering it as a simple silicate melt, such as a slag.

The writer's reply to these conclusions is limited to a wish that there would be less profound theorizing in the solitude of studies, and more active inspection of the actual exposures in the field and of sections under the microscope.

STORGANGEN DEPOSIT NEAR JOSSING FJORD, NORWAY

The deposits in Norway have never been described adequately in English, and the writer is indebted to Dr. Gustav Jebsen, of A/S Titan Co., and to officials of the National Lead Co. who have seen the property, for the following information. The Storgangen deposit differs from smaller deposits near Egersund, but which are in the same mass of anorthosite, in that it is a mixture of ilmenite and magnetite, whereas the other ores are hematite-ilmenite ores like those of Quebec.

The Storgangen body is 1200 meters long and has an average width of 50 meters. The ore averages about 40 pct ilmenite with some magnetite, the gangue being hypersthene, augite, and andesine; $3\frac{1}{2}$ tons of ore is required to produce a ton of concentrate, which assays about 44 pct TiO_2 , 35 pct FeO , and 12 pct Fe_2O_3 .

Since the deposit is only a few kilometers from Jossing Fjord, which has been converted to a deep-water port and to which it is connected by a railroad, bulk shipping is facilitated. Furthermore, since usually there is excess shipping capacity westbound from Europe, the Norwegian ore can be delivered to eastern seaboard ports of the United States very cheaply. This favorable shipping condition adds greatly to the commercial importance of the large Norwegian deposit.

The concentrate made from the ore has been used extensively for pigment manufacture on the Continent of Europe and in England, in manufacturing processes similar to those employed in the United States. The concentrate should be an excellent metallurgical feed, although it might have to be sintered for use in reverberatory or electric furnaces.

VIRGINIA TITANIUM DEPOSITS

The titanium deposits in Virginia^{7,13,42a,52-55,67} occur in an area between Charlottesville and Lynchburg, lying mostly in Nelson County; hence the designation "nelsonite," which was assigned to some of the unusual titaniferous rocks found there. A "nelsonite" is a dikelike or lens-shaped body of rock containing abundant ilmenite or rutile (or both) and apatite, with biotite, chlorite, and actinolite as gangue minerals.

Ross says that the dominant country rock is a gneissic quartz monzonite of pre-Cambrian age, which has been intruded by a feldspathic rock that originally was composed only of andesine (which contained microscopic lenses of antiperthitic microcline). This intrusive mass is roughly elliptical in shape, being about 13 miles long and $2\frac{1}{2}$ miles in greatest width and having a total area of about 22 square miles. The rock is related to a typical anorthosite and, although the feldspar is more sodic than most rocks of that type, the name seems to be applicable.

The ores and associated gangue minerals were deposited by invading solutions that are believed to have been derived from a highly ferromagnesian rock, which probably was a differentiate from the same primary magma as the anorthosite. The chemical factors seem to have been rather simple in character. Some of the higher-grade ore bodies are dike intrusions in the gneiss.

An important deposit of disseminated ore is near the village of Roseland, where the American Rutile Co. has been operating a quarry for years in the white feldspathic rock in which rutile, and some ilmenite, forms about 5 pct by weight of the mass. For a long time, the production from this quarry supplied practically the country's requirements of rutile.

There are many nelsonite bodies, a few of which are large. The surface of one of these, on the Warwick Farm near Piney River, had been deeply weathered, giving a deep soil zone of "soft ore," which permitted cheap open-quarry mining, without blasting, and easy crushing of the ore. The Vanadium Corporation started an operation on this deposit in the early '30s and built a titanium oxide plant near-by. The apatite was recovered and converted to monocalcium phosphate, the essential ingredient of Southern hot biscuits, and an important local business in this chemical was developed. Recently, the pigment plant has been acquired by the American Cyanamid Company.

The Virginia ilmenite contains magnetite as graphic intergrowths. Mechanical separation of the magnetite was not possible but leaching with weak acid raised the TiO_2 by removal of iron. (See analyses, Table 2.)

The reserves of the soft ore, assaying about 17 pct TiO_2 , are several million tons. The fresh nelsonites assay about 14 pct TiO_2 and constitute a very large reserve, but will require underground mining. Some smaller bodies of nelsonite are of higher grade.

Moore^{42a} believes that nelsonites found in Amherst County, which adjoins Nelson County, are genetically related to a granodiorite that had intruded the Lovingsston gneiss. The nelsonite dikes came in as magmatic intrusions, but they were later intensely altered hydrothermally. He concedes the possibility that the first stage of formation of the dikes was possibly a replacement of solid rock by solutions, but he thinks the evidence is against this conclusion.

HEMATITE-ILMENITE ORES

Hematite-ilmenite ores occur in several places in the world and form the largest known reserves of titaniferous ores. The hematite occurs as gashlike veinlets oriented along crystallographic planes in the ilmenite; formed, presumably, by unscrambling from solid solution. What physical-chemical conditions favored this manner of formation of these iron and titanium minerals, instead of the more widespread ilmenite-magnetite, has not yet been explained.

Small and as yet unworked deposits in anorthosite occur in southern Norway near Kyland, east of Egersund. These are dikelike in form, probably being emplaced along structural lines. The ore is about the same grade as that in the near-by Storgangen deposit, and hence much less massive than the two Quebec ores to be next described. Polished sections of the ilmenite from Kyland are practically indistinguishable from the Quebec sections, except in grain size (see Fig XXXII-B, ref. 66).

The comparatively small deposits near St. Urbain, Quebec, were described by Mawdsley³⁷ and Warren,⁶⁵ and also in an earlier article by the writer.²¹ They occur also in anorthosite, in a small area in the Parish of St. Jerome, about 7 miles north of the town of Baie St. Paul, which in turn is about 60 miles east of the city of Quebec. The largest lenses are very small by comparison with the Romaine River deposits, next described. One, identified as No. 619, from the lot number on which it occurs, is about 600 ft long and 75 to 100 ft wide. A neighboring lens, called the Coulomb, is a little smaller. The ore, after some hand sorting during mining, runs about 39 to 40 pct TiO_2 .

A tremendous boost to the reserves of titaniferous ores came very recently as a result of the most careful and painstaking geological ex-

ploration. The original find occurred in 1940 when Joseph A. Retty,^{3b,50} of the Quebec Bureau of Mines, found several deposits along the shores of a lake called Allard during a season of reconnaissance geological exploration of the country around the lower Romaine River Valley, Seigneurie de Mingan, Saguenay County. The Romaine River discharges into the Gulf of St. Lawrence from its north shore near the fishing village of Havre St. Pierre. The management of the Kennecott Copper Co. became interested in the potential importance of the area and financed a thorough geological exploration, on the theory that where there was so much "smoke" there must be some "fire." The finding in June 1946 of the huge deposit near Lac Petit Pas, and another near by in a cliff above a lake to which they gave the appropriate name of TiO, is a tribute to the careful work done under the resident geologist, Paul Hammond. Subsequent drilling has proved that the Petit Pas deposit is a massive lens, roughly circular in area and probably tabular in form, since it, like the others in the area, has a bottom surface roughly flat, at least throughout much of its explored sections. The reserve of ore proven runs into scores of millions of tons. The Petit Pas ore averages about 85 pct combined oxides of iron and titanium. The smaller, but still large, body called the Cliff, above Lake TiO, is a little higher grade and should yield ore that need not be concentrated for a metallurgical feed except by a little selective mining.

Subsequent geophysical exploration by the aerial magnetometer testified to the thoroughness of the work of the ground crew, since no new deposits were found. Unexpectedly, the massive deposits give a strong negative magnetic anomaly (both on the ground and from the air) whereas disseminated deposits, and the granite contact zone, give a positive anomaly. The St. Urbain ores, both massive and disseminated, and all titaniferous magnetites, as far as the writer knows, give positive anomalies.

The mineral associations and contact relations of the ore minerals in the deposits in the Romaine River area are so similar to those at St. Urbain that the writer feels that these deposits are also pneumatolytic replacements, although Kennecott geologists are known to favor a pyromagmatic origin.

NORTH CAROLINA ILMENITE

Although a number of deposits of both rutile and ilmenite ore are known in the state of North Carolina, only one has been worked commercially. This deposit is referred to generally as the Yadkin Valley deposit. It lies about 13 miles north of the town of Lenoir, in Caldwell County.

The ore occurs as a dike-like intrusion in the Carolina gneiss and consists of ilmenite and rutile in a micaceous gangue formed of chlorite,

talc, and mica. The mica carries abundant fine rutile, which is lost in concentrating the ore.

The ore zone is parallel to the gneissic structure, which there strikes northeast and dips southeast at an angle of about 45° . Quarrying started at a place where the ore zone makes a dip slope of the hill and, being about 30 ft thick, could be removed cheaply. The ore as mined runs about 30 to 35 pct TiO_2 . As the ore dike extends to the northeast, it becomes much thinner and much lower in TiO_2 .

An operation was started about 1940 by Herbert Rhodes to supply titanium ore to the Glidden Paint Co. He developed a process of flotation that involves a thorough and double desliming, which removes much of the micaceous gangue and some of the ilmenite, so that the overall recovery is low. Two-stage flotation is employed; ilmenite and some mica are floated with oleic acid, then mica is floated away from the ilmenite by the use of a cationic reagent. Test work on this flotation was described by McMurray.³⁶

The concentrate is exceptionally high grade for a rock ilmenite, running 49 to 52 pct TiO_2 .

ROCK DEPOSITS OF TITANIFEROUS MAGNETITE OF MINOR IMMEDIATE COMMERCIAL IMPORTANCE

A deposit north of Laramie, Wyoming,^{4,15,20} has attracted attention for many years because some of the ore carries 20 pct TiO_2 , but the geographical location is unattractive for commercial development and recent exploration by Frey²⁰ has indicated that the deposits are not as large as had been thought by earlier observers.

Perhaps the largest deposits within the continental United States are those in the San Gabriel Mountains, Los Angeles County, California. The ore occurs as disseminations in a gabbroic facies of an anorthosite but the average is too low grade to justify the enormous capital expenditure required to work them. The average grade of the crude ore—a grade that may be applicable to enormous tonnages—is about 4.5 pct TiO_2 . Deposits occur around Pole Canyon, Rattlesnake Canyon, Sand Canyon, Iron Mountain, and at other places, mostly on the north flank of the Range. They have been described recently by Paul C. Bateman, in an unpublished thesis for his degree at the University of California at Los Angeles, and by Moorhouse,⁴³ who advanced evidence for a pneumatolytic origin of the ore.

Other deposits occur in nearly every one of the western states, of which noteworthy examples are Montana,⁶⁹ Wichita Mountains of Oklahoma,⁴⁰ Boulder County, Colorado,²⁸ and the San Juan district, Colorado,⁵⁸ where a deposit with perovskite is reported. Deposits of titaniferous magnetite occur in the Duluth gabbro in Minnesota,⁹ in the Seven Island area of Quebec,¹⁸ and in many foreign countries.^{25,27a,56,71} Russia is said to have enormous deposits.^{30,49,62}

Beach Sand Deposits

The bulk of the production of titanium ores, both of arizonite and rutile (though not of ilmenite), has come from placer deposits, of which ocean beach sands are the most important. These occur in many parts of the world but a survey shows that those of commercial importance are all on continental land masses, and all near or in the tropics or in areas that at some time had a period of peneplanation under conditions that probably were subtropical, or at least that favored deep weathering, and hence solution of magnetite and most iron silicates. Deposits of high-grade arizonite do not occur in places where mechanical disintegration of the rocks has not been preceded by chemical decay. There are plenty of black beaches on the shores of volcanic islands but the principal black mineral in those sands is augite and the most abundant titaniferous mineral is a mixed grain of ilmenite-magnetite.

It was found that the following steps in geological history are common to all the commercial deposits of beach sand:

1. A "hinterland" of crystalline rocks in which the arizonite, rutile, and zircon were accessory constituents.
2. A period of peneplanation during which a deep soil zone formed in which all magnetite was decomposed. In India, this was a time of laterization, in which a deep red soil was formed; in places, pisolitic.
3. Uplift, and rapid erosion of the soil zone, and quick dumping into the sea of the products of stream erosion, without intermediate deposition in long stream channels, which would have resulted in dispersal and infinite dilution (the reasons why the United States deposits are very low grade). High mountains that lie close to the sea as a result of faulting account for the rapid erosion and velocity of the rivers. The coast of Brazil, Sierra Leone, and that of Travancore, India, testify to faulting (probably in the latter case repeated) parallel to the present coast.
4. In all places except India, an intermediate stage fitted into the history, involving deposition of the heavy minerals into a coastal plain sediment, which later was elevated and eroded, causing the heavy minerals to be concentrated further. In India, there is a thin layer of Tertiary sediments but concentration of the ilmenite from them has not been an important contribution to the total on the beaches. The stage has been important in both North and South America, and in Australia.
5. Subsidence of the coast was followed by the familiar process of shore straightening, which caused the formation of alongshore sand bars, extending from headland to headland. As the shore currents moved sands along the coast, ocean swells began to drag bottom when the bar was built high enough, causing breakers to form, and the force of these waves carried minerals of lighter specific gravity into the deep

water on the landward side of the bar, leaving the heavy minerals, not so easily moved, behind on the bar itself.

6. Elevation of the coast permitted attacks on the partially concentrated sands in bars or on coastal plain sediments, by the waves or by the wind or by both. Black beaches result when waves reach back at times of storm, undercut cliffs of coastal plain sediments, or of dune or bar ridges, digest the fallen blocks, and wash the minerals of low specific gravity out to sea. Some of the light minerals are blown from the beaches by wind and form dunes behind the beaches, leaving the heavy minerals concentrated on the beaches. The heavy minerals remain about where they fall.

With variations, this has been the history in India, Senegal, Sierra Leone, Brazil, Florida, and on the eastern shore of Australia. The later history in Florida is obscure, and obviously the wind has had a great deal more to do with the concentration on Trail Ridge in Clay County than it has at any other place except possibly in the state of Rio Grande do Norte, in Brazil.

TRAVANCORE, INDIA

The black beaches of Travancore supplied the bulk of arizonite used by the pigment manufacturers prior to World War II. Interference to shipping because of the war, and more recently by political hindrances in the state itself, has relegated "Indian ilmenite" to a subordinate position in the trade. Development of other more dependable sources, even of ilmenite of poorer quality, is likely to keep the Indian production at a lower level than formerly, in spite of the expanding volume of ore required by industry.

The crystalline rocks of Travancore are basic gneisses, given Scandinavian names, but American petrologists would call them simply gabbro or diorite gneisses. The "ilmenite" came originally from these rocks, having been concentrated in the deep red soil that formed on the surface by tropical weathering.

Major rivers brought the products of erosion of the red soil down to the sea, but later the drowning of their mouths put an end to the delivery into the sea of any sand detritus. The beach deposits came from sandbars built up along the "drowned" coast, using as source material the sand at hand, in which there was a minor concentration of heavy minerals as a result of the weathering and stream action.

There are two beach deposits in Travancore—one near a place called Manavalakurichi (a name abbreviated by the English community to "MK") on the south coast, only a short distance west of the extreme southern tip of India, Cape Comorin; the other and larger deposit, about 80 miles north, on a barrier beach that extends from the mouth of Neendakara Inlet to the mouth of Kayankulum Inlet, a distance of 15 miles.

Production started at MK around 1906, not for the ilmenite, for which there was no use at the time, but for monazite, a mineral found also in the sand, originally in considerable concentration.

The MK deposit is a modern beach placer, resulting from the destruction by the waves, during the period of the southwest monsoon, of dunes built on an elevated bar or spit carrying small percentages of heavy minerals. The localization of the deposit at that place results from vagaries of stream diversion and changes in level, which make a most interesting study in physiographic history.* The deposit lies across an abandoned channel of a tributary of the Paralayar River. This channel is occupied now by an insignificant creek called the Valleyar. The Paralayar once flowed past Arumanullur and Bhutapandi and a tributary heading above Padmanabhapuram flowed past Sungankada and past the present salt pans at Rajakkamanagolam, which lie in its abandoned channel. The branch in the present channel of the Valleyar River joined the tributary and together they formed the main Paralayar, to the east, in a channel now submerged by the subsidence of the coast.†

The submergence brought the shore line inland beyond its present position at MK, forming an estuary of the Vallayar channel, and brought the sea into the Nagercoil embayment, an area now covered by recent calcareous marine deposits, lying a few feet above sea level.

About the same time, the lower end of the Paralayar River was captured by the Tambraparni and diverted north, leaving wind gaps at Mekkod, now used by the Puttanar aqueduct, and at Sungankada, now used by the Anandan aqueduct and the main state highway to Nagercoil. The headland at Muttam east of MK became an important factor in the localization of the deposit. Before the recent uplift, it was an island in the sea. A spit formed, joining it to the mainland at Colachel across the estuary of the Vallayar, and on the building of this spit, the heavy minerals were concentrated by the waves dragging bottom and washing the light minerals over into the land-side lagoon. Recent emergence of 15 to 25 ft occurred and raised the spit above the sea. The waves went to work on the partial concentration of the heavy minerals on the spit and in dunes formed by the wind on top of it.

As emergence continued, the shore retreated seaward and beach concentrations made earlier were buried under dunes that blew over them. For years, one of the operating companies, Hopkin and Williams (Travancore), Ltd., dug down through the dunes and found rich layers of these old beaches, which they mined.

The accessible reserves at MK are approaching exhaustion and,

* See Indian Survey Sheets 58 H₃, H₄, H₇, H₈.

† Sounding along the coast are not sufficiently close together to mark this channel but the shallow water extends out for at least 4 miles. A rock 4 miles off MK is a navigational hazard, as it is awash at low tide.

since the MK "ilmenite" is lower in TiO_2 than that on the northern beach, most of the operations have been conducted at the latter place since about 1932.

The northern beach is called the Quilon (pronounced K̄wī'lon), after the old city of that name that lies a few miles to the south. The concentrating plants have centered around the villages of Chavra and Kovilthottam (the English spelling of Tamil and Malayallam words varies with the interpreter), and the shipping off the beach has been done at Kovilthottam.

The beach is a barrier beach, extending parallel to the old shore in front of the mouths of two rather large rivers—the Panalur at Neendakara and Pallikal Todu. The latter river formerly had its mouth about at latitude $9^{\circ}1'N$ (sheet 58 C/12) but recently has been diverted north to Kayankalum Inlet, latitude $9^{\circ}8'N$ (sheet 58 C/8). That the coast is still rising is confirmed by the fact that when Marco Polo visited Quilon "junks from Cathay, carrying 700 souls" were in the harbor; now the dugout canoes used by the fishermen are about the largest boats than can go out over the bar across the channel, at the entrance to Neendakara estuary.

Behind the barrier beach is a back-water channel used as an inter-coastal waterway—a waterway similar in physical features, if not in place names and adjoining vegetation, with many sections of that along the United States Atlantic Coast.

The ocean beach is black, with layers carrying 80 pct heavy mineral, and dunes on the elevated bar are gray, with 40 to 50 pct heavy mineral, and below them are old beaches buried under dunes formed before the shore retreated, which are as rich as those now washed by the waves. The canal side of the elevated bar and the adjoining mainland is covered with clay extensively cultivated for paddy (rice), and the bottom of the canal and lagoons is covered with a thick layer of river mud (not ocean sand). If buried older beaches underlie the "paddy" fields, the reserves may be very much greater than surface indications suggest. This contingency of buried seams could add to the reserves, perhaps substantially, but the facts that the coast lies only a few feet above sea level for a wide belt, and that inland, where the ground rises a few feet, the higher surface is the "terra rosa" or old laterite soils, lead to the conclusion that the emergence has not been considerable. The river-laid mud on the "paddy" fields indicates no recent resubmergence; hence sands found at greater depth presumably will never have received any appreciable wave or wind concentration.* No systematic drilling below water table has been done but a few borings have been

* The writer belabors this point because expansive claims are made in regard to the buried reserves.

made, in which a depth of about 12 ft of sand of workable grade was found below water level.

A very considerable part of the barrier beach is covered by densely populated fishing villages, such as one called Cheriayeckal, and mining has been confined to the open beach and to unsettled private dune land purchased for the purpose by the mining companies, of which there are four—Travancore Minerals Company, Ltd., Hopkin and Williams (Travancore), Ltd., F. X. Pereira and Sons, and Associated Minerals. Recent action by the State Government makes it a partner of the companies and probably will force the consolidation of the companies into one.

The maximum annual production from Travancore was 267,000 tons of ilmenite in 1940. Other than political restrictions, shipping, rather than production facilities, is a limiting factor, since there are only about 175 days in the year when roadstead loading is possible. The effort of loading an average of 1400 tons or more a day off the beaches into dugout canoes, and from them into sailing lighters called "dhonies," is about the maximum possible. The ilmenite is sacked but the bags are emptied into the hold of the ship. Alternative shipment via back-water canal 100 miles to the port of Cochin is limited by the number of slow-moving and shallow-draft "wallums" available, and powered equipment cannot operate in the canals unless and until the canals are deepened to a minimum of 5 ft.

CEYLON

A deposit on the east coast of Ceylon could have been of importance were the ilmenite of a quality comparable to the Travancore variety. The deposit lies about 35 miles north of Trincomallee and extends from the mouth of the Kokkilai Lagoon south for 4 miles. The sand carries ilmenite 75 pct and zircon and garnet 25 pct. Coates¹² says that the reserve is at least three million tons of heavy mineral, not including that in lower-grade dunes back of the beach.

BRAZIL

Brazil has deposits of heavy minerals on its coast wherever the bottom beds of the coastal plain are exposed to attack by the sea, or were so exposed prior to a recent 5-meter uplift. Deposits extend in closely spaced groups from Barra de Itabapoana, in the northeast corner of the state of Rio de Janeiro, to a place called Saí, north of Vitoria in the state of Espirito Santo. A little farther north, around the mouth of the Rio Dôce, one of the major rivers of that section, is a large delta deposit, with black minerals formed by the mechanical carving of the big river down to the fresh unweathered gneisses. Although the de-

posits on the delta are large, the black mineral, even after elimination of the magnetite, analyzes only 44 pct TiO_2 .

Another pair of deposits occurs in southern Bahia, at places called Guaratiba and Comoxatiba. Then for a long distance to the northeast the beds exposed at the coast are younger members of the Tertiary, in which very little heavy mineral is found since all the rich accumulation from deep weathering on the Cretaceous peneplain was dumped into the first member of the series.

In Rio Grande do Norte, the basal member of the coastal plain is Cretaceous, and large deposits of low-grade sand have been found at Cunhaú, Tibáu, and Tambáu, all south of Natal.

The deposits in Brazil are as follows:

1. Elevated sand bars.
2. Elevated beaches, where waves attacked the Tertiary cliffs.
3. Modern placers, where the sea has cut inland past the elevated shore and reached into the old cliff or *barreira*.
4. Dune deposits, formed by the wind action on the elevated bars and beaches.

The deposit at Saí is an example of No. 2, Comoxatiba of No. 3, and Cunhaú of No. 4. Nearly all of the others belong to the first class. Most of these bars are 20 to 40 meters wide, and vary in length from a few score meters to several kilometers. The maximum depth is not greater than 4 meters, except very locally. The grade of the crude sand in the bars is high, the average of many being in excess of 40 pct heavy mineral.

Although some production of these deposits has been maintained for a number of years, particularly around Guarapary, by a company, formerly French, now called Mibra (Monazita e Ilmenita do Brasil), the relatively low quality of the Brazilian ilmenite and the inaccessibility of the deposits to ports usable by overseas vessels have been deterrents. Furthermore, Brazilian mining law has discouraged the investment of foreign capital.

The average Brazilian "ilmenite" assays only about 56.5 pct TiO_2 , although that in Bahia is better, being up to 61 pct, and hence as good as the Indian or Floridian.

AUSTRALIA

Deposits of sands in Australia^{6,19,68} occur in northeastern New South Wales and southeastern Queensland that are elevated storm-line deposits; i.e., elevated beaches formed where storms once attacked the dunes. The sands consist of about 60 pct zircon, 25 pct rutile, and 15 pct ilmenite.

Since the ilmenite is of poor quality, being high in chromium oxide and an ilmenite (rather than arizonite) with only about 50 pct TiO_2 , and the plants are not situated favorably for bulk transportation, ilmenite has not been produced in Australia in quantity. These operations supplied very considerable amounts of rutile and zircon during World War II, and can continue to do so, price permitting.

N. H. Fisher¹⁹ has the following to say about the Australian deposits:

"The most important known deposits of what are commonly referred to as the beach-sand minerals are situated along the most easterly part of the Australian coast, between Southport, 17 miles north of the Queensland-New South Wales border, and Ballina, 50 miles south of the border, and most of the production has come from this area.

"Submergence of the order of 100 to 200 ft at the close of the Pleistocene period left the pre-existing hills as promontories and the valleys as deep inlets. Wave action has built baybars and sandspits in a northerly direction from the headlands, and lakes and marshes have formed between these bars and the initial postsubmergence coastline. These lakes and swamps have been or are being filled in by river-borne sediments or wind-blown sand. Beasley⁶ has presented evidence that suggests a recent emergence of the coast line of about 10 ft. The evidence for this belief is the presence of a black-sand seam $\frac{1}{3}$ mile inland and 17 ft above sea level, and although it is not entirely certain that this seam is of beach formation and owes nothing to wind-blown concentration, other evidence supports the suggestion of recent emergence. Such emergence would undoubtedly aid the formation of bars and sandspits and the easterly progress of the beach front, leaving a series of parallel dunes.

"However, the relative abundance and richness of the deposits in the area from Ballina to Stradbroke Island must be related to the existence of a comparatively prolific source of zircon, rutile, and ilmenite in the mainland rocks of the area. The main immediate source has usually been assumed to be the fresh-water sandstones of the Clarence Series of Triassic-Jurassic age, with some contribution of ilmenite from the basalts of the Ballina-Point Danger area. The original source of most of the zircon, rutile, monazite, and part of the ilmenite is undoubtedly the extensive Permian granite masses of the New England area, which extend from just north of the Queensland border south for 250 miles. After erosion of the granite, these minerals have eventually found their way to the beaches, either via the Clarence sandstones or more directly by way of the present major streams of the North Coast area, which rise in or adjacent to the granite. The principal stream is the Clarence River, which enters the sea near Yamba, 96 miles south of the border, and this river, together with the Richmond, which comes out at Ballina (or their ancestral streams), is considered to have been the main avenue of delivery of heavy minerals to the ocean sands."

FLORIDA

"Ilmenite" was produced from Pablo Beach, near Ponta Vedra, south of Jacksonville Beach, from storm-line deposits, as early as 1922,³⁷ and for a number of years local accumulations along the shores of Indian River were worked by "Riz" Mineral, an operation moved later to an elevated bar south of Vero Beach and now moved to a storm-line deposit on the ocean front near Vero Beach. Some accumulation of heavy minerals occurs in many parts of Florida, all the way from Amelia Island in the northeast to Santa Rosa Island in the far western part of the state. So far, only two places have been found where large deposits of workable grade occur—an elevated bar east of Jacksonville and south of the St. Johns River and an old ridge, called Trail Ridge. On the west flank of the ridge are repeated layers of storm-line deposits and wind-blown enrichments of heavy minerals. The location of the deposits is in and near the site of Camp Blanding, and east of Starke. The average grade of sand in both places is extremely low, and only the fact that cheap mining by dredging can be employed, and the development of the Humphreys spiral concentrator, which permits rapid concentration, has made the operation possible. The ilmenite, moreover, particularly that from Trail Ridge, is of excellent quality.

Operation began on the bar east of Jacksonville about 1942, by the Rutile Mining Co., a subsidiary of the Titanium Alloy Manufacturing Co., and shortly thereafter the Humphreys Gold Corporation was engaged to mine for that company under contract. The Humphreys management, which was experienced in placer operations, moved in a big dredge and built a large plant for gravity concentration, employing their spiral devices. The spiral concentrate is treated in a dry mill employing electrostatic and magnetic separation. The finding of the larger Trail Ridge deposit is a result of exploration by the U. S. Bureau of Mines under the able direction of J. R. Thoenen. In 1947, E. I. du Pont de Nemours and Co. leased several sections from the Florida Armory Board and engaged the Humphreys Gold Corporation to construct and operate a plant capable of producing about 100,000 tons of titanium minerals annually. Production began in 1949.

TITANIFEROUS IRON SANDS

Although the beaches of many volcanic islands are black, the only deposits of this kind that are really important are in Japan and New Zealand.^{26,27,70} The resources of New Zealand are very large but the TiO_2 content is low. Furthermore, the sands contain a large amount of mixed grains and of pyroxene with included fragments of magnetite, which render them magnetic and make them electrical conductors. This hinders the concentration of the titaniferous magnetite grains into a

product sufficiently low in gangue to be a smelter feed for the production of a titanium slag of acceptable grade. Furthermore, the lack of coal in the North Island, and the small market for pig iron in New Zealand, are deterring factors to immediate development.

Although titaniferous iron sands occur near several old volcanic centers on the North Island of New Zealand, the biggest deposits are on the Taranaki coast, between Wanganui and Hawera, and on the west coast near Mokau. The titaniferous magnetite found at Taranaki was blown out of Mount Egmont near New Plymouth and concentrated out of the ash by streams and wind. The largest reserves are in Pleistocene beds, although recent dunes are extensive. The total reserve may be in the order of two hundred million tons of magnetite in sands carrying over 25 pct magnetite. The magnetite when concentrated away from most of the mixed grains assays about 8 pct TiO_2 . Very large reserves of lower-grade sands exist.

Stream Placers

Stream placers and residual deposits in soils containing rutile have been worked in a few places. A deposit of minor importance in the United States is in Clay County, North Carolina, $3\frac{1}{2}$ miles east of Hayesville on U. S. highway 64. The district is called "Shooting Creek." The underlying rock is mica schist. The overburden is said to run about 50 lb of ilmenite and rutile to the yard. A small operation has been under way. The area of "pay dirt" probably covers several hundred acres.

Similar deposits have been worked in Brazil,^{2,3} which probably collectively constitute the world's largest sources of rutile, although most of the deposits are low grade and a long way from the coast. Those in the state of Goaz have been described by Leonardos³³ as residual and stream placers over schists and phyllites. Those in Ceara were worked actively during the war. They have been described by Chambers.¹⁰ Some of the mineral is intergrown with ilmenite, so that the TiO_2 content is low for rutile. The climate in Ceara is arid and the gravels, which are found in dry river beds, over metamorphic rocks, are worked by a system of dry placer mining—essentially a screening operation. A picture in Colonel Chambers' report shows a workman with a gourd half filled with rutile crystals representing the results of a morning's work—implying that the kilos of rutile per cubic meter are few.

Deposits, probably similar in character, occur in the Cameroons.

MINING AND CONCENTRATING

The rock ores produced at Tahawus, New York; St. Urbain, Quebec, and Jossing Fjord, Norway, are quarried or mined, and no especial features mark the mining operation. The rock at Tahawus is so tough that 90 pct gelatin is used in quarry blasting.^{6a}

The sands of India are gathered by hand, using a hoelike tool called a *mommiti*. Production in Brazil is still mostly by hand methods. In Australia, one company uses a $\frac{1}{8}$ -yd Ruston-Bucyrus trench digger and another uses a road scraper pulled by a caterpillar tractor; still another uses horse-drawn *fresnoes*. Only in Florida is a large-scale mechanical equipment used—a 15-in. suction dredge. At Trail Ridge, a still larger dredge (20-in.) is employed.

Concentration of ilmenite from rock ores has been by gravity and magnetic methods. At the MacIntyre development in the Adirondacks, the ore is crushed through a 60-in. jaw and further broken through a 7-ft Symons cone. This discharge is screened and products plus 2-in. and plus $\frac{3}{4}$ -in. are passed over magnetic pulleys, thus rejecting some of the feed as a "cobber tails." The cobber concentrate is further crushed in 5-ft Symons cones and rescreened, the oversize products going back to the cobbing plant. The minus $\frac{3}{4}$ -in. product is ground in rod mills to minus 28-mesh and is fed to Crockett magnets for elimination of the magnetite. The Crockett tails are sized in Dorrco hydrosizers and the plus 65-mesh is fed to tables. Most of the minus 65-mesh goes to a flotation plant where a final concentrate is made, running about 46 pct TiO_2 . The wet table concentrate is dried in Millville driers and fed to Wetherill magnetic separators, producing a concentrate about 44.5 pct TiO_2 .

The concentration of sand ores is by gravity, magnetic, and electrostatic methods. In India, where the head feed is very rich in ilmenite, a magnetic separation on belt-type machines produces a final concentrate of the more magnetic ilmenite in one pass, and reduces the bulk by 50 pct, plus or minus. The lesser magnetic product is tabled to eliminate quartz and sillimanite, redried, and then chased around through Humboldt roll separators, over home-made air jigs, and over other high-intensity magnetic separators to produce a second ilmenite concentrate. A rutile concentrate and a zircon product are produced from ilmenite tailings on electrostatic machines. Monazite is enriched on the air jigs and concentrated on belt-type magnets. Sillimanite is recovered from table tailings by flotation and by electrostatic methods.

In Australia, the crude sand is tabled and the gravity concentrate is treated in three different ways by several operators. Rutile-Zircon, Ltd., floats the product and makes separate concentrates of rutile and zircon in that way. The National Lead Company's subsidiary at Cudgen, N.S.W., follows the Florida practice, and separates the electrical conductors, rutile and ilmenite, from the nonconducting silicates. Then both rutile and zircon are separately cleaned on induction-type magnetic separators. Other operators, including Rutile Sands Proprietary and Metal Recoveries, Ltd., give the table concentrate a magnetic separation first on Australian-made magnets of the glass disk type and clean the non-magnetic product on static machines of the Sutton type.

In Florida, the low-grade crude sand is concentrated in three stages in Humphreys spirals.^{22,24,32a} The concentrate, after drying, passes through several stages of electrostatic separation in machines designed by J. Hall Carpenter, which use a very high voltage impressed on a piano wire. A constant flow of charged ions from the wire to the grounded feeding rotor pass through the conductors, ilmenite and rutile, without displacing them from the normal trajectory. Nonconductors pick up a charge and are "pinned" to the feeding rotor, from which they are brushed off at the four o'clock position by a brush.

Conductors are split on induction-roll magnetic separators into an ilmenite concentrate and a rutile-rich product, which is cleaned further on statics and other magnets. The nonconducting fraction of the Florida sand carries a large amount of worthless silicates of intermediate gravity, principally staurolite and, at Jacksonville, epidote. This fraction is put back over a separate spiral plant, producing a final gravity concentrate that is 90 pct zircon. This product is dried and cleaned on electrostatic machines and magnetic separators to a high-quality product.

Australian products that are not clean enough to meet specifications in the United States are recleaned here. Foote Mineral Co. has designed an electrostatic table, which is in use at Exton, Pennsylvania, and Orefraction, at Pittsburgh, Pennsylvania, uses another version of an electrostatic table, but the feed is heated to dull red heat before the separation.

Metallurgical treatment of titaniferous ores has been attempted by many investigators over many years,⁶⁰ for the purpose of recovering iron only. Such ores are now used to a modest extent by blending with nontitaniferous ores to reduce the TiO_2 content to about 2 pct. Recently attempts to make a titaniferous slag, with or without simultaneous recovery of the iron in a usable form, have been made. The problem has not been easy. "Ringing" (i.e., building up of a ring of slag on kiln walls) has ended attempts to use a rotary kiln and the slag is too viscous to use with regular practice in a blast furnace. O'Dea⁴⁴ has described a reduction with carbon, after roasting with Na_2CO_3 .

The problem of smelting of titaniferous iron ores has been solved only in the past few years and announcements have come during 1948 and 1949. Four papers from technologists of the National Lead Co., one of them reporting a cooperative effort with the U. S. Bureau of Mines, were delivered at the meeting of the American Institute of Mining and Metallurgical Engineers in February 1949.^{3a} They disclosed electric smelting of titaniferous magnetites with dolomite and limestone to produce a low-silicon pig iron and a calcium-magnesium-iron-aluminum polytitanate slag of 60 to 70 pct TiO_2 . This slag, which can be dissolved in the usual acids applied to ilmenite in the production of titania pigments, is richer in titania than the ilmenites and arizonites now used, and hence there will be a saving in acid consumed and much

less soluble metal sulphates will have to be crystallized and discharged to waste.

Coincident with the development of this slag by the National Lead Co., another slag has been made on a semi-works scale, which is also an iron polytitanate with 70 and even 75 pct TiO_2 . This slag has resulted from research by the Kennecott Copper Co. in collaboration with New Jersey Zinc Co., and on which there is yet no technical literature. Since the slag has been offered for sale to most of the titania pigment producers, its nature is generally known. Apparently, during electric smelting of the ore of the Quebec type, low-silicon pig iron is made and insufficient carbon is used to reduce all the iron in the ore, so that enough ferrous oxide is left to flux the titania and make a ferrous dititanate slag. This slag is also treatable in the usual titania pigment processes and likewise permits economies on acid and reduces volume of heavy metal salts of low or no value.

Although not yet in commercial operation, a metallurgical process probably is the next major development in the treatment of titaniferous ores, and ores not now usable, or usable only at a penalty, will become very desirable raw materials. These will include the Romaine River and St. Urbain ores of Quebec, the Norwegian ore, the Brazilian ore, and perhaps even ores very low in TiO_2 , such as the New Zealand sands or the Swedish ore of the Kuickjokk district, with 11 pct TiO_2 .

IMPORTS, CONSUMPTION AND QUALITY OF ORES

The figures for production and imports and for consumption, taken from U. S. Bureau of Mines statistics, are shown in Table 1.

Analyses of numerous concentrates from miscellaneous ores are shown in Table 2.

USES

Uses of ilmenite and rutile are listed in Table 3.

The largest use for titanium oxide is as a pigment. This is produced by several companies in the United States and abroad. Leading producers are the National Lead Co., with plants at Sayreville, New Jersey, and East St. Louis, Illinois; E. I. du Pont de Nemours and Co., with plants at Baltimore, Maryland, and Edge Moor, Delaware; American Cyanamid Co., with plants at Piney River, Virginia, and Gloucester, New Jersey; Glidden Paint Co., with a plant at Baltimore; Titangesell Schaft, G.M.B.H., Leverkusen, Germany; British Titanium Pigments, at Billingham, England, and National Titanium Pigments, at Luton, Bedfordshire, England; Fabrique de Produit Chimique, at Thann and Mulhouse, France; and Societa Anonima Titanium, a subsidiary of Societa Montecatini Generale per l'Industria Mineraria e Chimica, at Milano, Italy.

TABLE 1—*World Production of Ilmenite and Rutile*
METRIC TONS

Year	Ilmenite								Rutile						
	Aus- tra- lia	Brazil	Canada	Feder- ated Malay States	British India	Norway	Portu- gal	Sen- egal	United States	India	Aus- tra- lia	Brazil	Nor- way	Cam- eroon	United States
1932					50,853	13,841						35	30		
1933	559			204	53,828	23,213	645	310				96	56		
1934			1,835	51	76,855	26,306	434	540				116	247	45	
1935		287	2,076	2,540	129,085	37,984	385	3,810					124	55	
1936		9	2,328	10,470	142,721	67,194	530	3,912				721	198	102	
1937	681	234	3,837	6,352	183,952	67,333	1,456	3,176		1,141		654	187	118	
1938	330	317	188	6,566	256,247	62,724	568	8,436		457		215	124	159	
1939	683	10	3,351	11,098	260,027 ^a	55,027	409		13,247	716		489	166	503	2,620
1940	2,270	12	4,114	2,596	267,376		899	5,798	18,750	934	1,641	499	156	2,839	
1941	3,779	4,471	11,477		131,111	61,086	798	895	21,135	1,891	3,816	2,369	172	1,399	2,402
1942	4,588		9,100		49,977	60,713			70,042	2,295	5,503	4,615	77	2,153	3,617
1943	5,717		62,992		38,041		120		184,657	2,396	6,483	4,557	116	2,750	6,279
1944	7,287	3,250	30,820		102,412				252,749	1,672	8,843	1,564	85	2,902	6,513
1945		5,000	12,834		162,879 ^a		301		279,880			160		1,046	6,761
1946					197,480 ^a				256,230						
1947					238,204 ^a				294,500 ^b						

^a U. S. imports only.^b Partly estimated.

TABLE 2—*Analyses of Titanium Minerals*

Minerals	Composition, Pct					
	TiO ₂	Fe	FeO	Fe ₂ O ₃	Cr ₂ O ₃	V ₂ O ₅
Beach and other placer ilmenites:						
Australian:						
Cudgen, New South Wales....	51.2	32.2	27.2	15.9	2.50	0.21
North Carolina:						
Albemarle Sound.....	50.5	34.4	34.9	10.4	0.04	0.56
Shooting Creek.....	55.5		28.0	12.5	N.D.	N.D.
Arkansas, Tokio Formation.....	47.7	32.1	27.2	15.5	0.53	0.24
Malayan tin placer residues.....	53.4	31.1	32.6	8.2	0.01	0.04
Rock ilmenites:						
Adirondack 3-yr composite.....	44.4	32.9	37.3	5.43	0.006	0.13
Norwegian 9000-ton shipment....	44.0	35.3	35.4	11.0	0.01	0.30
Canadian:						
St. Urbain, Coulomb 500-ton shipment.....	38.8	35.7	28.7	19.0	0.11	0.38
"Lot 619" composite.....	42.1	39.0	31.5	20.8	0.09	0.38
North Carolina:						
Yadkin Valley, 500 tons.....	51.6	31.3	34.9	5.91	0.08	0.57
Virginia:						
Magnetically concentrated...	43.5	38.1	35.0	15.6	0.06	0.19
Magnetically concentrated—acid washed (same sample)	46.7	38.7	37.1	14.1	0.08	0.23
Georgia:						
Elberton dist. first concentrate.....	50.50	35.92	39.60	7.31	N.D.	N.D.
California:						
San Gabriel Mts., laboratory concentrate.....	47.3	36.5	38.7	9.1	0.04	0.21
Finland:						
Sample submitted by Finnish Trade Commission.....	48.8	37.6	38.9	10.5	0.01	0.77
Leucoxenes:						
India, "weathered Quilon".....	67.5	7.51	0.86	9.77	N.D.	N.D.
Florida, Trail Ridge second magnetic fraction.....	82.1		1.60	9.0	N.D.	N.D.
Rutile:						
North Carolina:						
Shooting Creek.....	89.6		1.5	2.1		
Norway:						
Kragerö.....	95.6		3.67			
Arkansas.....	92.36	1.77			0.31	
Australia.....	97.13					
Cameroon.....	96.70					
Brazil, Ceara.....	93.76				4.07	

TABLE 2—(Continued)

Minerals	Composition, Pct					
	TiO ₂	Fe	FeO	Fe ₂ O ₃	Cr ₂ O ₃	V ₂ O ₅
Arizonites:						
Travancore:						
Average "Quilon".....	60.4	24.7	9.55	24.6	0.17	0.36
Brazil:						
Mibra, 500-ton shipment from Guarapary.....	58.9	25.1	6.62	28.6	0.05	0.45
Itabapoana, Praia Mosés, first concentrate.....	56.55	27.45	4.88	33.31	0.03	0.36
Average of six beaches ^a	56.57	26.88	5.59	31.96	0.045	0.293
Guaratiba.....	59.84	24.64	2.78	32.12	0.068	0.41
Florida:						
Jacksonville, average ship- ment.....	60.3	22.7	5.59	26.3	N.D.	N.D.
Trail Ridge, 500-lb sample...	64.0		4.8	26.0		
Arizonite-ilmenite mixture:						
Travancore:						
"MK".....	54.1	30.6	25.6	15.3	0.09	0.23
Brazil:						
Ponta da Fruta.....	53.20	31.80	23.70	19.10	0.06	0.22
Pedra Virada, Rio Grande do Norte.....	55.93	31.25	25.65	16.11	0.04	0.35
Ceylon:						
Pullmodai.....	54.8	31.2	18.7	23.8	0.16	0.50

^a Guaratiba, Saí, Carapebús, Guarapary, Ponta da Fruta, Praia Mosés.

Titanium oxide of pigment quality is manufactured principally by attacking arizonite or ilmenite with concentrated sulphuric acid.^{44a} All ferric iron present must be reduced with iron scrap so that the iron sulphate formed is all in the ferrous state. The titanium is dissolved in water as a basic titanium sulphate, and after selective crystallization of the ferrous sulphate, the basic titanium sulphate is precipitated by hydrolysis, filtered, calcined to the oxide, and ground to pigment size.

The du Pont company has built a plant to produce the oxide by another route.

Rutile is made into welding-rod formulations and ground as a ceramic pigment. Titanium Alloy Manufacturing Co., at Niagara Falls, Orefracation at Pittsburgh, Pennsylvania, and Foote Mineral Co., Exton, Pennsylvania, are producers of rutile products.

Titanium tetrachloride is used as a smoke screen, and for skywriting, since it hydrolyzes in moist air to the oxide. Titanium carbide was made in Germany for cutting tools.³⁴

TABLE 3—Consumption of Ilmenite and Rutile by Uses, 1945-1947
SHORT TONS

Product	Ilmenite		Rutile	
	Gross Weight	TiO ₂ Content	Gross Weight	TiO ₂ Content
1945				
Pigments.....	371,691	183,195		
Welding-rod coatings.....	115	62	7,813	7,344
Alloys and carbide.....	8,611	3,976	1,923	1,750
Ceramics.....			34	30
Miscellaneous ^a	761	347	21	20
Total.....	381,178	187,580	9,791	9,144
1946				
Pigments.....	399,042	200,352		
Welding-rod coatings.....	105	57	5,990	5,600
Alloys and carbid.....	4,685	2,025	1,035	966
Ceramics.....			75	72
Miscellaneous ^a	451	229	34	32
Total.....	404,283	202,663	7,134	6,670
1947				
Pigments ^b		233,914		

^a Consists of ilmenite used as a steel flux and rutile used in lamp electrode coatings and as a steel deoxidizer.

^b Other consumption not available.

TITANIUM METAL

At the time of preparation of this chapter, the production of metallic titanium has advanced well into the state of semi-works operation, and the metal is being made in several plants, both government and private.^{14,72-81} Many other laboratories are working on its production and possibilities of its use, and on the alloys that can be made from it. The interest that has been stimulated in it is tremendous, because of its great strength in proportion to its weight, and its extreme resistance to corrosion by sea water.

The metal, which has defied reduction by simple processes, is made now by several methods. Du Pont and the Bureau of Mines use a process of magnesium reduction, which was developed by Kroll in Germany in 1932. This method involves the reduction of titanium tetrachloride by reaction with magnesium metal. The titanium so formed is in the sponge or powder form, which is converted to ingots by melting in an inert atmosphere or in a high vacuum. A reduction of the chloride with metallic sodium is employed in the Hunter process. A method of making very pure titanium was developed by Van Arkel and de Boer.

In this process, crude metallic titanium, nonductile because of absorbed oxygen and nitrogen, is reacted with iodine in an evacuated vessel to form volatile iodides, which are decomposed on a heated body, such as a tungsten or titanium filament, to form a coherent mass of titanium and liberate the iodine, which resumes its function as a carrier.

Dominion Magnesium, Ltd., of Toronto, has announced a direct reduction of the oxide to metallic powder by the Pidgeon process, which the management believes should be cheaper than the reaction of the chloride with magnesium.

Titanium offers some new and valuable properties. It is a strong, medium weight, corrosion-resistant metal, with a melting point 300°F higher than iron. It retains its strength at moderately elevated temperatures, where aluminum and magnesium lose much of theirs. The metal's ability to hold its strength without much expansion at temperatures between 300° and 800°F makes it a leading candidate for jet-turbine blades, which must clear their housings within close tolerances. The development of alloys is only just starting, but several with outstanding properties have been developed.

At the time of writing, titanium is in the exciting state when anything may come out of it. Westinghouse engineers⁷⁸ see the possibilities of revolutionary effects upon design, engineering, and performance, particularly in the fields of aeronautics and reciprocating machinery, where high operating temperatures must be endured. Nevertheless, at the moment, its corrosion resistance is perhaps its most interesting property.

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Acknowledgment

In the preparation of the bibliography, much assistance was afforded by a bibliography prepared by Charles S. Du Mont, of the Battelle Memorial Institute, Columbus, Ohio, entitled "Bibliography on Titanium—Its Production, Properties and Uses." The references cited here are only a fraction of those listed by Mr. Du Mont.

CHAPTER 50

TRIPOLI

By ROBERT W. METCALF*

THE name "tripoli" is used to designate a number of more or less similar types of silica of sedimentary origin. Usually they are spoken of as "soft" silicas, and are light, very fine grained, porous, and friable. Structure is microcrystalline or cryptocrystalline. The deposits are the residual product of weathering and occur in massive form, either blocky or in friable masses.

Tripoli is the end product of the weathering of siliceous limestones, cherty limestones, or cherts. Weathering removes the calcium carbonate, leaving a finely divided siliceous residue to which the name "tripoli" has been applied. Authorities differ as to whether the chert accumulates first and is converted into tripoli or the tripoli is derived by direct decay from various forms of silica during initial weathering of the limestone.

It has also been asserted that tripolis were formed in situ in essentially their present condition as a flocculent, colloidal silica, but it is now believed by most geologists that varying degrees of pressure, combined with one or more methods of origin, have influenced the characteristics of the deposits.

Considerable confusion has existed as to what constitutes tripoli. Owing to the similarity of names, tripolite, a type of diatomaceous earth found originally in Tripoli in northern Africa, has been erroneously called tripoli. Tripoli, however, contains no diatoms, the distinguishing characteristic of diatomaceous earth.

The material mined in the Missouri-Oklahoma area has been considered by the trade to be the type material, and many feel that the term "tripoli" should more properly be restricted to the product of this region. Although also designated as soft silica, it would be less misleading, perhaps, if the siliceous material mined in southern Illinois were called amorphous silica. Both the Missouri-Oklahoma and Illinois materials are very high in silica. Different in composition, as it is very much lower in silica content than tripoli or amorphous silica, yet included under the classification of tripoli in Bureau of Mines statistical data, is the small but important output of rottenstone in Lycoming County, Pennsylvania. The principal justification for grouping these three types of silica is similarity of use.

* Nonmetal Economics Branch, Bureau of Mines, Washington, D. C.

COMPOSITION AND PHYSICAL PROPERTIES

Composition—The tripoli of Missouri-Oklahoma and the amorphous silica from Illinois are practically pure silica, as they contain 96 to 99+ pct of SiO_2 , the remainder being chiefly ignition loss and small quantities of alumina, iron, lime, soda, and potash. Analyses of commercially marketed tripoli and amorphous silica are given in Table 1. The chemical composition as indicated may be considered as typical, although material of varying characteristics may be produced from each of the districts shown. (These data are taken for the most part from Heinz' study of the tripoli industry.²⁴)

TABLE 1—Chemical Composition of Tripoli and Soft Silica

Constituent	Composition, Pct					
	Illinois	Arkansas	West Tenn. Valley	East Tenn., Georgia	Missouri-Oklahoma	
					Cream	Rose
Figures Quoted in 1937 ^a						
SiO ₂	99.44	99.72	98.92	93-98	97.70	98.00
Al ₂ O ₃	0.22	0.067	0.46	1.0-1.4	0.838	0.19
Fe ₂ O ₃	0.14	0.003	0.07	0.22-1.6	0.282	0.73
CaO.....		0.090	0.37	tr-0.30	0.001	tr
MgO.....		0.001		tr-0.20	0.014	tr
Na ₂ O-K ₂ O.....					0.148	0.29
TiO ₂				tr-0.20	0.059	
MnO.....					0.002	
H ₂ O (clay).....					0.099	
Ignition loss.....	0.25	0.120		0.3-0.7	0.501	0.50

More Recent Analyses of Cream and Rose Tripoli

Constituent	Cream, Pct	Rose, Pct	Constituent	Cream, Pct	Rose, Pct
Silica.....	97.50	94.40	Lime.....	0.15	None
Alumina.....	0.15	2.73	Magnesia.....	tr	tr
Iron oxide.....	1.87	1.87	Ignition loss.....	1.00	1.00

^a The chemical analyses of the Missouri-Oklahoma tripoli are by C. V. Millar, chemist, Joplin, Mo.; the other figures, from producers in the various districts.²⁴

Properties—The physical characteristics of tripoli are much more important than the chemical composition. Even the minor minerals associated with the silica in tripoli should perhaps not be regarded as impurities, since they are mainly surface coatings or fill the finely cellular openings and impart certain physical properties applicable to specific uses for this mineral.

The color of tripoli varies from white to cream, brown, rose, and red, and is the result of the adsorption of iron from surface waters percolating through the deposits. For the Seneca product, mined in Missouri and Oklahoma, commercial varieties are designated as cream and rose.

Fusion point for cream-colored tripoli is cone 33 and that for rose tripoli is cone 31. The index of refraction is 1.54. True specific gravity varies widely, between 2.15 and 2.63. The apparent specific gravity fluctuates greatly, varying from 1.19 to 0.69, according to fineness of the grade. The weight per cubic foot may vary from 35 lb for raw or crude tripoli to as much as 55 lb for the powdered material. Some variation also occurs in the unit weight under different conditions—a short ton of tripoli in place occupies about 30 cu ft; broken or in drying sheds, 45 cu ft; powdered and packed for shipment, about 33 cu ft. Fracture is uneven to conchoidal. Tripoli from this district is thus light in weight and very porous; the porosity of the crude material is about 45 pct.

Oil absorption for the rose product averages around 51 pct and in the neighborhood of 53 for cream-colored material. Water absorption of crude averages about 38 pct and that of powdered tripoli about 52 pct. The rate of absorption varies considerably, however, and a cube of natural cream tripoli will take up 50 pct of its weight in one minute while a cube of rose-colored tripoli may not absorb the same percentage of its weight in less than an hour. Blocks from even the more compact beds can be crushed easily in the hand. The individual grains, however, have a hardness sufficient to scratch steel.

Of particular value from a marketing standpoint are its microcrystalline particles and the high surface area due to the extreme porosity, 1 lb of finely ground material probably possessing a minimum of 6000 sq ft of area.

The rottenstone mined in Pennsylvania is somewhat heavier in unit weight and lower in silica content than other products included in this report. Composition approximates 60 pct silica, 17 pct alumina, 8 pct alkalis, and 9 pct iron oxide, plus small amounts of moisture, lime, and magnesia. The material apparently is a ferruginous and siliceous shale, having properties rendering it suitable as an abrasive or filler.

DISTRIBUTION OF DEPOSITS

United States

Deposits of tripoli in the United States occur principally in the South and Southwest. The larger reserves are in Missouri, Oklahoma, and southern Illinois. It is found also in more or less extensive deposits in Alabama, Arkansas, Georgia, Mississippi, and Tennessee. Rottenstone has been mined only in Pennsylvania.

Alabama—Tripoli is found in Lauderdale County in northwestern Alabama and also somewhat farther southwest along the east side

of Bear Creek nearly to Margerum, Colbert County, as a part of a belt extending from Wayne County, Tennessee, through Alabama into northeastern Mississippi. In the Bear Creek area, a good grade of white tripoli occurs near Riverton and Tredegar. Screen analysis of this material indicates that 53.30 pct will pass a 200-mesh screen and 50.70 pct will pass a 300-mesh screen. A proposed method of preparation includes drying and grinding in a tube mill—lined with silex and using flint pebbles—to such a fineness that 90 pct will pass a 200-mesh screen, the grading to be accomplished in an air separator. These deposits have not been mined for many years.

Arkansas—Tripoli has been mined and processed near Hot Springs, Garland County, Arkansas although for many years production has been entirely from the northeastern corner of the state, at Rogers, Benton County. In the latter region, the tripoli apparently is derived from decomposition of the cherty or siliceous limestone beds in the upper part of the Boone formation of Mississippian age. This formation spreads over a considerable part of northern and northwestern Arkansas. A number of deposits other than that mined at Rogers occur in Washington and Madison Counties, adjoining Benton County, and in Baxter County. In the west-central portion of the state appear tripoli beds that have been altered from the Arkansas novaculite formation. Counties in which the tripoli-bearing strata occur include Garland, Hot Spring, Montgomery, Pike, and Polk, with small-scale operations in past years confined practically to locations near Hot Springs, Garland County, and Butterfield, Hot Spring County. Deposits in southwestern Montgomery County and Pike County, particularly, extend over a sizable area and are said to be good quality.

Georgia—The occurrence of tripoli in Georgia is confined to the northwestern part of the state, in Bartow, Catoosa, Chattooga, Floyd, Gilmer, Murray, Polk, Walker, and Whitfield Counties. The first discovery of this material in the United States was reported in 1857 near Dalton, Whitfield County. No production has been reported for many years, but output was obtained chiefly from Chattooga, Walker, and Whitfield Counties.

The Georgia tripoli deposits lie largely in the upper part of the Knox dolomite of Cambro-Ordovician age and are associated with chert beds. Tripoli also occurs in Georgia associated with the Bangor limestone of Mississippian age, the Shady limestone of Cambrian age, and the Murphy marble of pre-Cambrian age. The tripoli in this state varies in color from the white material found in Catoosa and Chattooga Counties to the cream and buff varieties in Walker and Whitfield Counties. Georgia tripoli is of the amorphous silica type.

Illinois—Amorphous silica deposits in Illinois are within an area of Devonian strata in the southern part of the state, in western Union

and northern Alexander Counties. These strata trend north and south through the hilly and rough terrain characteristic of this unglaciated region and cover an oxbow-shaped area approximately 30 miles long and 5 miles wide, spreading to about 10 miles in width in northern Alexander County. The Devonian here consists of interbedded limestones, generally with green or brown shades or slates and cherts. The so-called Clear Creek cherts contain the amorphous (soft) silica deposits as well as hard cherts or novaculites. The latter have been quarried by open-pit methods and used extensively throughout this area for road building; the amorphous silica occurs in thin beds and is recovered by underground mining.

All the workable deposits are nearly horizontal, seldom dipping more than 5° . The strata largely are unconsolidated and look not unlike layers of hardened or congealed flour. The beds are greatly altered or decomposed and comprise alternate pure white veins up to about 6 ft in thickness and dark red or bluish gray material.

Mississippi—Tripoli in Mississippi occurs as a part of the Iuka formation of the Lower (Iowa) series in the Mississippian system. This formation forms the surface terrain over a large part of northeastern Tishomingo County and is the southwestward extension of the tripoli deposits in Alabama and Tennessee. Exposures are few and the tripoli is not abundant except in the vicinity of an old silica mine southwest of Eastport. The topography is broken and rugged because of the limestone weathering in this area. When mined, the tripoli was taken down a small valley by tram and thence by Bear Creek to a plant in Alabama on the Riverton Branch of the Southern Railway, where it was ground and prepared for market. The tripoli of Mississippi is of the "soft" silica variety and is generally pure white.

Missouri-Oklahoma—The tripoli deposits in the Missouri-Oklahoma region lie along or near the contiguous borders of the two states and are structurally similar. They are a part of the Boone formation of Mississippian geological age, which consists of a group of alternating beds of limestone and chert with an average overall thickness of 200 to 350 ft. The principal beds occur in the hilly, weathered limestone country in Ottawa County, near Gate, Oklahoma, and Seneca, Missouri; in the northeastern corner of Oklahoma and in adjacent Newton County, Missouri; spread over an area of less than 100 square miles. The deposits are horizontal and are found near the tops of broad flat-topped ridges. The tripoli beds vary from 4 to 15 ft in thickness and as a rule are not excessively folded or faulted. The easily removed overburden generally comprises 4 to 8 ft of loose soil, gravel, and decomposed tripoli and does not exceed 12 ft in commercially workable areas. East and south of Seneca, the cover, and frequently the tripoli also, becomes thicker. With depth, the tripoli becomes harder and less marketable.

Tennessee—The deposits of tripoli in Tennessee extend northeast to southwest diagonally through Wayne County, into Lauderdale County, Alabama, and continue on both sides of Bear Creek into Colbert County, Alabama, and Tishomingo County, Mississippi. Tripoli also occurs in southeastern Hardin County, Tennessee.

Tripoli is found all along this comparatively narrow belt but the largest deposits are in three general localities: the region between Waynesboro and Collinwood, Wayne County, and near Stout, Wayne and Hardin Counties, Tennessee; in Lauderdale County, Alabama, and along Bear Creek in Alabama and Mississippi.

The tripoli occurs in the southwestern part of the Highland Rim geologic province of Tennessee, a generally flat plateau dissected by the Tennessee River and its tributaries largely into a series of narrow, flat-topped ridges between steep-sided valleys. The tripoli outcrops along the sides and in the bottoms of the stream valleys in this rugged topography. At many places the exposures are easily spotted, as the tripoli is heavily compacted and tends to form vertical banks that can be recognized even though covered with vegetation and detrital matter.

The tripoli in this region is pure white, except for occasional brown streaks caused by iron oxide. It is very soft and crumbles easily in the fingers. The dry powder, crushed easily in the hand, will readily pass a 100-mesh screen, and small quantities will pass 200-mesh openings. When dry, the material is very light.

The mineral occurs mainly at the top of the Fort Payne cherty limestone and at the base of the Warsaw limestone. The grains of the tripoli from the Fort Wayne formation are comparatively large, and a considerable amount of cherty fragments is intermixed with the true tripoli. Grains from the Warsaw beds, on the other hand, although very irregular, naturally are finely and evenly sized. Most of the deposits showing material of commercial grade apparently were found in the Warsaw beds.

Typical of the deposits in Tennessee are those of Hog Hollow, in the Waynesboro-Collinwood district, and Second Creek in the Stout area. The former is 4 miles south of Waynesboro, at the head of Hog Creek. The outcrop measures more than 300 ft, has an average thickness of 30 ft, and is entirely within the Warsaw formation. Reserves in this district are the largest in this series of deposits. Quality seems satisfactory and highway and rail facilities are ample.

In the Second Creek area, the maximum thickness of the tripoli is about 60 ft and the length of the outcrop along a road cut is about $\frac{3}{10}$ mile. The product is soft, easily crushed, and pure white. Average analysis indicates a silica content of about 96 pct, iron oxide 1 pct, and other (including alumina), 4 pct. Another road cut $\frac{1}{2}$ mile away on the west side of Second Creek exposes tripoli at the same elevation, of

similar quality and extent. Again the deposits seem definitely to be derived from the Warsaw limestone.

Deposits in the Knox formation in Bradley County, at Black Fox, near Cleveland, also have been worked in the past. Large deposits in the Knox formation occur near Greeneville, Greene County. Tripoli, or as locally known, "rottenstone," formerly was mined near Butler, Johnson County, in the northeastern corner of the state. Tripoli is known to occur in several counties in west central Tennessee, including Dickson, Humphreys, Lewis, and Perry.

Analyses of tripoli from Tennessee have been reported as shown in Table 2.

TABLE 2—*Analyses of Tripoli from Tennessee*

Constituent	Composition, Pct		
	1	2	3
Silica (SiO ₂).....	87.84	98.92	88.60
Alumina (Al ₂ O ₃).....	8.84	0.46	6.40
Iron oxide (FeO).....	0.66	0.07	0.22
Lime (CaO).....		0.37	0.57
Magnesia (MgO).....			2.02
Ignition loss.....	2.43		2.06

1. Black Fox mine, Cleveland, Bradley County (Bureau of Mines *Bull.* 266).

2. Central Silica Corp. (out of business), Collinwood, Wayne County; analysis by Tennessee Division of Geology.

3. Parsons mine, Decatur County; analysis by Tennessee Division of Geology.

Pennsylvania—Rottenstone is mined in the United States only in Pennsylvania, near Antes Fort and Muncy, Lycoming County. It occurs as the weathered insoluble siliceous residue of the black calcareous Trenton limestone or shale.

World Deposits

Deposits of tripoli and rottenstone in foreign countries are not extensive. The former, however, has been produced on a small scale in France, Germany, Portugal, and Spain.

French output of tripoli has never been very large and has been obtained in conjunction with oil-shale deposits. Production in Portugal in recent years usually has been well under a thousand tons annually. Output in Spain has centered in the two provinces of Albacete and Jaén (chiefly in the latter), in the southeastern part of the country, and has increased substantially in recent years. The tripoli, occurring in horizontal beds for the most part, in Miocene and Eocene measures, is interstratified with clay and is very white, spongy, and extremely porous

when pure. Generally though, clay and small quantities of calcium, iron oxide, and other elements are present. It is used largely in the manufacture of soap for the Spanish market.

A true rottenstone mined in England occurs near Hull, in the Yoredale rocks of Derbyshire, and also in Wales and Belgium. This material, a residual product of the weathering and disintegration of siliceous and argillaceous limestone, carries more impurities and less silica than the Missouri-Oklahoma tripoli. Its chemical composition varies within the following approximate limits: silica, 80 to 85 pct; alumina, 4 to 15 pct; carbon, 5 to 10 pct; iron oxides, 5 to 10 pct; plus small amounts of lime. It is a soft, earthy, very light, finely divided light to olive-gray product. An analysis of a good quality rottenstone of this type, occurring southwest of Cwm Haffes, Glen Tawe, South Wales, is as follows:⁷³ silica, 80.82 pct; alumina, 5.82; ferric oxide, 3.79; lime, 1.43; magnesia, 0.88; soda, 0.30; potash, 1.40. Uses include polishing wood and metal, and as a paste, for rubbing down or smoothing painted and varnished surfaces. In normal times, this rottenstone is exported to the United States and to Europe and provides one of the abrasive bases in certain English paste and liquid metal polishes.

POLITICAL AND COMMERCIAL CONTROL

The production of tripoli has not been affected by international commercial agreements to any great extent, particularly since the United States apparently possesses the only sizable export surplus and under normal conditions ships perhaps 35 pct of its output to foreign destinations. Although specific quantities exported to the various countries are not available, it is understood that the most important overseas market for tripoli as a buffing and polishing agent is Great Britain. Shipments are sent also to Belgium, Holland, France, Germany, and other European nations. Exports have been made to South and Central American countries, Africa, Australia, New Zealand, and India. The total volume of these foreign movements probably reaches several thousands of tons a year. With respect to duties on imports of this material into the United States, tripoli has always been on the free list.

English rottenstone has been imported into the United States in limited amounts and also was exported to European countries.

TRIPOLI MINING

United States

The mining of tripoli is comparatively simple and may be either by shaft or open-pit operation. Drilling, by hand or machine, follows no particular pattern and depends on prior experience in each area. Slow dynamite or black powder generally is employed in blasting, to reduce the proportion of fines, and the larger boulders, where found, are broken

by wedges and hammer or by sledges. In certain areas the rock is hand-loaded into tramcars and conveyed to the mill in various ways.

Arkansas—Mining of tripoli in Arkansas is by shaft. The mine portals generally are some distance from the outcrop, and tunnels must be driven through considerable unproductive strata. The tunnels are timbered and the rooms opening out into workable areas have dome-shaped roofs for better support and safety. The rock is loaded into metal "cans" or skips, hoisted to the surface and dumped into hoppers, from which it is trucked to the mill.

Georgia—Many of the tripoli or amorphous-silica deposits in Georgia are overlain by only 2 to 6 ft of overburden and have been mined by open-pit workings. The crude material was shot down either by single or multiple benches, sorted for color, and dried. Some mines in Walker and Whitfield Counties, however, were worked by underground methods. The latter have long since been abandoned and now are practically inaccessible. The product largely was shipped as untreated or unprocessed silica.

Illinois—Present mining is on a modified room-and-pillar system, sometimes called a checkerboard or square-work pattern. The mine portals almost invariably are on steep hillsides and the workings often extend hundreds of feet back into the hills. A series of parallel rooms 10 ft wide and 7 ft high is opened up, leaving 20-ft pillars to support the roof. To avoid timbering, the roof of each room is carefully arched, which affords additional protection from falling strata. After drilling, the crude material is shot down with black powder, the product ranging in size from 12 in. to flour. The freshly mined silica may contain up to about 25 pct combined and absorbed moisture. It has a cold, clammy feel, yet is only slightly moist to the touch. The darker beds—red or bluish gray in color—that alternate with the usable white layers have no commercial value. Because of streaks or veins, which occasionally appear irregularly in the commercially marketable white seams, mining in many otherwise profitable areas has been discontinued.

Missouri-Oklahoma—Mining in the Missouri-Oklahoma area is entirely by open-pit quarrying, a minimum of explosive being used in order to reduce shattering and pulverizing of the product. Formerly large amounts of even-textured tripoli were quarried without explosives. This material was carefully sorted and set aside for use in making filter stone, but these filter stones are no longer made. Most of the tripoli now mined is designated as "crush" and is sorted at the mine according to the three predominant colors occurring in the region—white, cream, and rose. In blasting, vertical holes spaced irregularly from 3 to 10 ft or more in depth are shot with black powder or slow dynamite. Wide variations in color of the tripoli in place require greater care in shooting to keep colors as segregated as possible. A large part, and

in some recent years all, of the tripoli mined in Oklahoma is ground and processed for sale at a mill in Seneca, Missouri. The crude tripoli as mined is wet and is taken to large drying sheds, where usually it remains 3 or 4 months. Then it is conveyed to the mill for grinding and preparation. One producer used to crush the rock to about 1 in. and put it through a mechanical drier instead of drying it in open-air sheds.

Tennessee—About 4 miles south of Waynesboro, Wayne County, a fine-grained, pure white tripoli containing more than 98 pct SiO_2 was drift-mined intermittently for many years. The raw material, which contained very little chert, was trucked 6 miles to Collinwood to a small, efficient plant and placed in storage sheds until milled. Tripoli formerly was mined and milled in Decatur County, near Parsons, where beds were said to be 100 ft thick, and in Bradley County, at Black Fox, near Cleveland.

Pennsylvania—The rottenstone occurring in Pennsylvania has been mined from open pits at Antes Fort and Muncy, Lycoming County. The material is crushed and dried before grinding.

PREPARATION FOR MARKET

The preparation of the soft silicas and tripoli involves grain-size reduction. The crude material, however, is sorted for color and texture and air-dried before shipment to the mill. The air-drying usually requires several weeks. Trade demands for certain qualities in the finished product complicate the milling routine, as grinding methods must be flexible enough to conform to individual requirements, such as abundance of superfines, uniform grain size, limits for presence of larger grains, or special grain-size distribution to give a certain oil-absorption number. Many mills, now inactive, followed flowsheets and milling procedures similar to those described in the following paragraphs.

Arkansas—The material in Arkansas was ground by wet classification at a mill at Rogers, Benton County. Special products could be produced by further processing the normal finely ground end product of milling. The tube mill employed in grinding was charged with the larger pieces of the badly fractured, decomposed chert. This "like" grinding medium was said to give satisfactory results. Sizes were segregated by means of a series of settling cones and the products were thickened and dried. The iron or other stains occurring along the fractures in the rock were largely removed by close regulation of the final water waste from the settling cones. Three chief products were made, designated as: Admix 025; white 325-400; and float 600. All passed 325-mesh sieves and each grade comprised 60 pct by weight of grains smaller than 10 microns.

No crushing was necessary at a mill formerly processing tripoli near Hot Springs, because of the natural fineness of the product in situ. The

material was trucked to the plant and, after drying, was conveyed directly to the first of two air separators, from which a 325-mesh product was recovered. From the other separator, mounted below, a 200-mesh grade was obtained in the ratio of about one part of 200-mesh material to three parts of 325-mesh. The finished products were sold to paint manufacturers and to makers of cleaning compounds.

Illinois—The white silica occurring in southern Illinois may be ground either wet or dry. In the wet-grinding process, one mill crushes the raw rock to about $\frac{1}{2}$ in., after which it is ground in tube mills using flint pebbles. In closed circuit with the tube mill are bowl classifiers. Two products for use in pigments are produced—fine-grained and superfine-grained. Another wet-grinding plant in southern Illinois produces several grades of silica ranging from 65 to 99.9 pct through 325-mesh. Alternatively, dry-grinding equipment with air classification may be employed.

Kansas—Although deposits of tripoli of commercial importance in Kansas are not known, there was a mill at one time at Baxter Springs, Cherokee County, in the extreme southeastern corner of the state, which treated material mined just over the line in Oklahoma. This mill was designed to process 50 tons per 8-hr shift but was idle for several years and has been dismantled.

Missouri-Oklahoma—The tripoli as it comes from the mine is hand-sorted for texture and color and separated into white, cream, and rose shades. This sorted material is then stacked or piled in open sheds to air-dry for approximately 3 to 6 months. The mills now operating in this area use dry preparation methods. The crude tripoli from the sheds undergoes coarse crushing either in hammer mills or in coal breakers followed by smooth rolls. The product that passes a $\frac{1}{4}$ -in. screen is then dried and pulverized, after which it passes to vibrating screens in closed circuit with the grinding mills. The darker colored tripoli presents fewer difficulties in processing than the lighter tinted material, as the latter, under certain conditions, becomes charged with static electricity and requires special precautions in screening technique.

Tripoli in this district is prepared in the following grain sizes and designations in the three colors, white, cream, and rose:

Air-float—all through 200-mesh and 98 pct through 325-mesh.

Parting—98 to 99 pct through 200-mesh.

Admix—90 pct through 200-mesh and 30 pct smaller than 10 microns.

Buffing—100 pct through 40-mesh and 80 to 85 pct through 200-mesh.

Extra fine admix—70 pct smaller than 10 microns.

Another, perhaps more prevalent, breakdown of the mill products is as follows:

Once ground, or minus 65-mesh, 87 pct through 200-mesh.

Double ground, or 110-mesh, 96 pct through 200-mesh.

Air-float, or all through 250-mesh and special air-float, or all through 300-mesh or finer.

Selected tripoli for filters was sawed into rough shapes and dried in sheds or by artificial heat. Disks, tubes, and cylinders were made on lathes or ground to exact dimensions on carborundum-surfaced wheels.

A generalized flowsheet for the Barnsdall Tripoli Corporation (now the American Tripoli Corporation), Seneca, Missouri, follows as closely as possible the description of the milling operations as reported by Trauffer⁷⁴ (Fig 1).

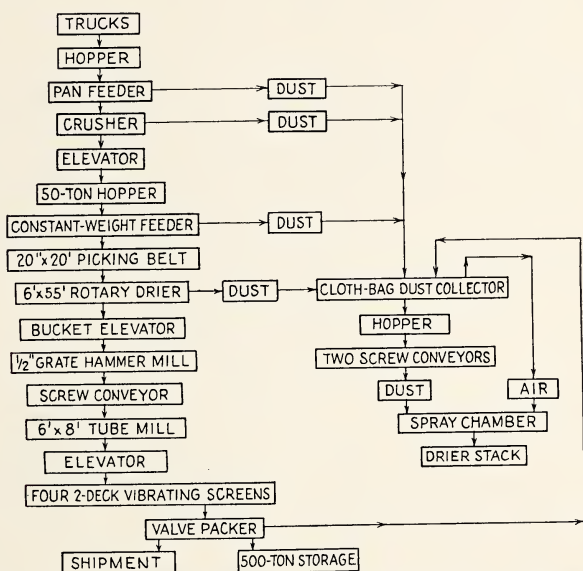


FIG 1—MILL FLOWSHEET, BARNSDALL TRIPOLI CORPORATION, SENECA, MISSOURI.

Tennessee—At an operation at Collinwood, Wayne County, Tennessee, now inactive, the crude tripoli was conveyed from the storage sheds to a rotary drying kiln, where the raw material was dried to about 9 pct moisture. A pebble mill in closed circuit with an air separator disintegrated the rock. The milled product was screened to remove unweathered chert fragments before it was sent to the air separator. The latter prepared four commercial grades of tripoli flour.

Tripoli was processed in the early '20s at Black Fox, near Cleveland, Bradley County. The crude rock was dried, passed through a $\frac{1}{4}$ -in. trommel, and conveyed to a Hardinge mill to break up lumps, and then to an air separator. From the air separator, four grades of

tripoli of each color were produced, although a much wider range of sizes was possible. The usual sizes marketed were:

100 pct through 200-mesh, 1 pct retained on 325-mesh.

100 pct through 200-mesh, 3 pct retained on 325-mesh.

100 pct through 200-mesh, 8 pct retained on 325-mesh.

100 pct through 140-mesh, 15 pct retained on 325-mesh.

Another mill was operated some years ago near Parsons, Decatur County, in the Fort Payne (Mississippian) formation. The tripoli was a white, fine-grained, soft, coherent material occurring in deposits said to be 100 ft thick. The processing equipment included a rotary drying kiln, revolving screens, tube mill, air separator, and accessory conveyors. The finished product could be classified as fine as 99.75 pct through 300-mesh. The mill had a rated capacity of $1\frac{1}{2}$ tons of ground tripoli per hour.

Pennsylvania—The rottenstone produced in Pennsylvania, after preliminary crushing and drying in a rotary drier, is ground and air-floated in Raymond air-separation equipment. The finely divided material is then conveyed to storage bins, bagged on automatic bagging machines, and shipped. Two chief products are prepared; a minus 250-mesh grade is consumed as a filler, largely in phonograph records, and a somewhat coarser grade is used for polishing.

PRODUCTION OF TRIPOLI

United States

Tripoli was first discovered about 1870 in southwestern Missouri and was partly developed in 1872. No production was made, however, until 1887, when new machinery was installed for fine grinding as well as for sawing, turning, and shaping block tripoli into the form of disks, cylinders, or tubes for water filters. Production was on a limited scale until 1892. During that year, the American Tripoli Co., of Carthage, Missouri, was organized. In 1905, it took over the plant of the Seneca Filter Works, which had built a mill at Seneca some 9 or 10 years before. The history of the tripoli industry in Missouri and later also in Oklahoma follows to a large extent the expansion and growth of the American Tripoli Co. and its successor, Barnsdall Tripoli Co. In 1947, the name was again changed to American Tripoli Corporation, almost the same as that adopted in 1892.

Separate statistics on tripoli output are not available before 1913, as diatomaceous earth and tripoli formerly were considered by many authorities to be the same or similar materials and were grouped in geological survey records of mineral production. Aside from scattered small output in the 1890s in Georgia, Virginia, and possibly Alabama, mining and preparation of tripoli up to 1914 were confined to Missouri.

Beginning in 1907 and continuing to the present, silica or "amorphous silica" produced in southern Illinois also has been included with the tripoli figures. Illinois is the only state for which a practically complete record of output since 1913 can be published, and these figures appear in Table 3. Production of so-called "rottenstone" was first reported in Pennsylvania in 1913 and a small output has been marketed each year thereafter. Initial mining of tripoli in Oklahoma came in 1914, of amorphous silica in Tennessee in 1924 (except for a small output in 1913), and of tripoli in Arkansas in 1929. For 1933 to 1941, inclusive, some production came from California, and in 1939 to 1941, amorphous silica was marketed from Texas. Georgia produced sporadically before 1936. The bulk of the output since 1907, however, has come from Illinois, Missouri, and Oklahoma.

Producers of tripoli, amorphous silica and rottenstone in 1946 were the following: Olive Branch Minerals Co., Cairo, Illinois (amorphous silica); Ozark Minerals Co., Cairo, Illinois (amorphous silica); American Tripoli Corporation, Seneca, Missouri, formerly Barnsdall Tripoli Corporation (tripoli); Penn Paint and Filler Co., Antes Fort, Pennsylvania (rottenstone); and Keystone Filler and Manufacturing Co., Muncy, Pennsylvania (rottenstone).

TABLE 3—*Production of Tripoli in the United States Compared with Factory Sales of Automobiles, 1913–1947*

Year	Tripoli Production, ^a Short Tons	Automobile Prod. (Factory Sales), ^b Number of Units	Year	Tripoli Production, ^a Short Tons	Automobile Prod. (Factory Sales), ^b Number of Units
1913	20,797	485,000	1931	26,682	2,389,738
1914	17,218	573,039	1932	14,775	1,370,678
1915	30,711	969,930	1933	20,878	1,920,057
1916	43,257	1,617,708	1934	20,529	2,753,111
1917	26,069	1,873,949	1935	27,375	3,946,934
1918	19,982	1,170,686	1936	28,487	4,454,115
1919	24,292	1,876,356	1937	34,936	4,808,974
1920	40,233	2,227,349	1938	22,188	2,489,085
1921	12,340	1,616,119	1939	33,474	3,577,292
1922	30,205	2,544,176	1940	30,212	4,472,286
1923	27,082	4,034,012	1941	29,301	4,840,503
1924	28,476	3,602,540	1942	17,536	1,041,524
1925	29,388	4,265,830	1943	14,912	699,828
1926	31,369	4,300,934	1944	18,425	738,134
1927	26,099	3,401,326	1945	18,247	725,215
1928	34,043	4,358,759	1946	28,955	3,089,507
1929	38,011	5,358,420	1947	34,578	4,797,587
1930	32,439	3,355,986			

^a Sources: Mineral Resources and Minerals Yearbook, U. S. Bureau of Mines.

^b Source: *Automotive Industry* (March 15, 1947) 96, 81.

TABLE 4—*Production and Value of Tripoli in the United States, 1913–1947*

Year	Total Tripoli		Illinois Only	
	Short Tons	Value	Short Tons	Value
1913	20,797 ^a	\$216,581 ^a	12,994	\$128,892
1914	17,218 ^a	142,428 ^a	10,387	59,394
1915	30,711	128,957 ^b	23,756	59,390 ^b
1916	43,257	215,216 ^b	33,187	82,968 ^b
1917	26,069	338,188	16,133	207,738
1918	19,982	199,854	12,004	100,126
1919	24,292	181,541	13,014	116,492
1920	40,233	569,677	24,458	360,651
1921	12,340	213,013	7,765	125,352
1922	30,205	316,728	18,747	194,371
1923	27,082	382,757	11,522	117,201
1924	28,476	389,409	13,466	116,188
1925	29,388	434,886	11,809	143,859
1926	31,369	523,609	11,948	192,483
1927	26,099	447,068	^c	^c
1928	34,043	555,576	^c	^c
1929	38,011	545,658	12,889	139,557
1930	32,439	507,505	9,954	116,307
1931	26,682	310,131	12,651	87,481
1932	14,775	232,700	6,097	84,795
1933	20,878	350,383	8,757	149,979
1934	20,529	329,356	7,417	119,418
1935	27,375	383,416	10,001	113,484
1936	28,487	391,878	10,981	138,063
1937	34,936	450,570	11,647	151,154
1938	22,188	329,081	8,141	117,107
1939	33,474	466,380	11,134	148,310
1940	30,212	366,569	11,521	155,576
1941	29,301	421,746	13,833	200,700
1942	17,536	272,428	12,575	203,390
1943	14,912	244,365	10,203	168,758
1944	18,425	501,863	12,031	205,732
1945	18,247 ^d	306,829 ^d	11,144	184,189
1946	28,955 ^d	549,099 ^d	15,631	321,600
1947	34,578 ^d	751,422 ^d	14,687	271,115

^a Includes output in Missouri as follows: 7529 short tons in 1913, \$83,995 and 6721 tons in 1914, \$81,434. Bureau of Mines not at liberty to publish totals for this state in later years.

^b Estimated at average value of crude material sold.

^c Bureau of Mines not at liberty to publish figures.

^d Comprises, in addition to Illinois, production in 1945–1947 from Missouri and Pennsylvania, as follows: 1945: Missouri, 6542 tons, \$114,188; Pennsylvania, 561 tons, \$8,452; 1946: Missouri, 12,180 tons, \$211,244; Pennsylvania, 1144 tons, \$16,255; 1947: Missouri, 19,375 tons, \$469,927; Pennsylvania, 516 tons, \$10,380.

World

Incomplete statistics of output of tripoli in foreign countries are available. In Spain and Portugal, the only two areas for which data in recent years have been reported, production generally has been small. Figures for these countries covering the period 1938 through 1946 are given in Table 5.

TABLE 5—*Production of Tripoli in Spain and Portugal*

Country	Metric Tons								
	1938	1939	1940	1941	1942	1943	1944	1945	1946
Spain.....	733	819	1,555	2,633	1,761	901	845	3,994	14,291
Portugal.....	842	361	720	2,915	988	485	163	1,203	387

SPECIFICATIONS

No recognized specifications or generally followed testing procedures exist with respect to any of the amorphous silica or tripoli products. Virtually all tests are based on previous experience and generally are entirely academic in character and scope. Some consumers use rough color "standards," based on matching samples in water or actual paint samples, or by previously established arbitrary criteria. Others specify a certain grit tolerance, to which, however, similar grades of apparently the same composition may react very differently. Loose dry-bulk weight may be determined by the Scott paint volumeter or settling tests can be made to establish distribution of subsieve sizes, a factor to which increasing attention is being given.

TABLE 6—*Production of Tripoli in the United States by Uses, 1935-1947*
SHORT TONS

Year	Abrasives	Concrete Admixtures	Fillers	Others	Total
1935	10,162	3,040	4,810	9,363	27,375
1936	16,943	2,074	3,107	6,363	28,487
1937	15,235	2,126	8,363	9,212	34,936
1938	8,097	2,170	5,584	6,337	22,188
1939	10,953	1,653	9,016	22,188	33,474
1940	10,279	1,683	8,451	9,799	30,212
1941	13,407	1,179	10,020	4,695	29,301
1942	5,447	754	8,887	2,448	17,536
1943	6,146	335	6,894	1,537	14,912
1944	13,218	316	3,423	1,468	18,425
1945	11,113	1	3,969	3,164	18,247
1946	21,206		4,450	3,299	28,955
1947	29,866		2,573	2,139	34,578

USES

Distribution of tripoli by uses was first presented in 1933. It is shown in Table 6 for 1935 through 1937. The proportion of the output consumed for various uses also is given but as a considerable portion of the total tonnage reported in each year was sold to dealers or jobbers, often the producers have no definite knowledge of the detailed end uses for which their product is consumed. In any event, it is believed that this table shows a reasonably accurate breakdown of the principal uses of tripoli. Sales of tripoli by uses are listed in Table 7.

The chief markets for tripoli are for abrasives, especially buffing and polishing compositions, and for inert and chemically stable fillers in a wide range of products. Sizable amounts are consumed in concrete admix and foundry facings. Minor quantities in various years have been reported used as an ingredient in oil-well drilling fluids, in pottery, and as filter blocks.

Buffing Compounds

One of the more important outlets of tripoli is its use in buffing compounds. In fact, the meaning of the term "tripoli composition" has been widened from the original designation as specifically a compound containing tripoli as the abrasive agent to include almost any abrasive material used for such a purpose. In recent years, however, the tripoli compound has consumed about 30 pct of the total tripoli production, and is used to cut down and to impart high luster to such metals as copper, brass, aluminum, and zinc. It is furnished in many grades from a dry, hard, "cut-and-color" composition to the straight greasy type of product for faster cutting action. The grades and applications of the burring and buffing compounds are varied by using different varieties of abrasives, such as emery, rouge, ground flint, ground sandstone, or fused alumina.

Spray Tripoli—One of the most important developments in the buffing trades in recent years has been the perfection of efficient spraying equipment, which, taken with the improvement in liquid compositions, has resulted in practicable methods for spraying buffing compositions onto the buffing wheel. Tripoli compositions known as "spray tripoli" were first developed in response to the need for such buffing in the nonferrous metal field. Spray tripoli comprises standard tripoli abrasive powder suspended in a grease or oil-base binder liquid at room temperatures, as contrasted with the usual solid bar or cake tripoli. The spray mechanism can be operated by a foot lever, leaving the operation with both hands free, or can be controlled automatically. Marked economy in consumption of buffing materials compared with the use of bars or cakes, the right amount of composition always present, much less wear on the buffs, easier cleaning and elimination of fire hazards

TABLE 7—*Sales of Tripoli by Uses, 1933-1947*

Year	Abrasives		Concrete Admixture		Filler		Oil-well Drilling	
	Short Tons	Value	Short Tons	Value	Short Tons	Value	Short Tons	Value
1933 ^a	7,034	\$109,185	866	\$13,703	1,907	\$41,163	<i>b</i>	<i>b</i>
1934 ^a	8,516	135,678	582	9,973	2,224	34,872	<i>b</i>	<i>b</i>
1935	10,162	159,134	3,040	42,450	4,810	65,445		
1936	16,943	247,948	2,074	27,834	3,107	38,454		
1937	15,235	228,373	2,126	21,627	8,363	108,285	<i>b</i>	<i>b</i>
1938	8,097	138,807	2,170	12,634	5,584	78,900		
1939	10,953	169,370	1,653	24,580	9,016	120,284	<i>b</i>	<i>b</i>
1940	10,279	119,609	1,683	15,895	8,451	113,862	1,840	\$16,949
1941	13,407	198,252	1,179	15,168	10,020	145,063	1,925	22,835
1942	5,447	85,013	754	8,895	8,887	144,055	<i>b</i>	<i>b</i>
1943	6,146	101,248	335	4,690	6,894	114,929		
1944	13,218	210,592	316	4,552	3,423	66,147	<i>b</i>	<i>b</i>
1945	11,113	188,262	1	18	3,969	65,569		
1946	21,206	406,620			4,450	89,721		
1947	29,866	654,232			2,573	47,640		

Year	Foundry Facing		Other Uses ³		Total	
	Short Tons	Value	Short Tons	Value	Short Tons	Value
1933 ^a	2,426	\$37,750	2,515	\$46,718	14,748	\$248,519
1934 ^a	2,477	38,231	2,459	33,024	16,258	251,778
1935	2,590	40,254	6,773	76,133	27,375	383,416
1936	<i>b</i>	<i>b</i>	6,363	77,642	28,487	391,878
1937	<i>b</i>	<i>b</i>	9,212	92,285	34,936	450,570
1938	<i>b</i>	<i>b</i>	6,337	98,740	22,188	329,081
1939	<i>b</i>	<i>b</i>	11,852	152,146	33,474	466,380
1940	<i>b</i>	<i>b</i>	7,959	100,254	30,212	366,569
1941	<i>b</i>	<i>b</i>	2,770	40,428	29,301	421,746
1942	<i>b</i>	<i>b</i>	2,448	34,465	17,536	272,428
1943	<i>b</i>	<i>b</i>	1,537	23,498	14,912	244,365
1944	<i>b</i>	<i>b</i>	1,468	20,572	18,425	301,863
1945	<i>b</i>	<i>b</i>	3,164	52,980	18,247	306,829
1946	<i>b</i>	<i>b</i>	3,299	52,758	28,955	549,099
1947	477	11,562	1,662	37,988	34,578	751,422

^a In 1933, includes 71 pct of total tonnage of tripoli sold; in 1934, includes 79 pct.

^b Included under "Other Uses."

^c Includes small tonnages used for filter blocks and in pottery.

due to high pressures and deficiency of composition, and no time lost from productive work while coating buffs, are among the advantages claimed. Additional savings would accrue from the elimination of the manufacture of odd sizes and shapes of bars or cakes and the consequent reduction of inventories.

Attention also is being directed to spray compositions containing abrasive powders not only for buffing nonferrous metals but also for buffing and coloring steel, stainless steel, plated surfaces, and various alloys.

Buffing compositions soluble in aqueous solutions have been developed. Materials with characteristics similar to stearic acid were used, instead of that substance, resulting in a buffing stick soluble or dispersible in aqueous solutions. Such soluble sticks are more expensive but the work can be cleaned much more quickly after their use, causing an actual decrease in overall cost.⁸⁶

Buffing Aluminum—The buffing and coloring of aluminum are accomplished by methods similar to those employed for other metals, except that the abrasives generally are finer and the wheel speeds slower, primarily because of the comparative softness of this metal. Buffing tends to bring out the high luster of the natural aluminum, while coloring enhances the luster and gives to the surface the highest possible gloss. Buffing and coloring wheels both have approximately the same dimensions—6 to 20-in. in diameter and $1\frac{1}{2}$ to 4 in. in thickness, depending on the size and shape of the material to be buffed or colored. The wheels vary in density and hardness according to the work to be done.

The abrasive generally used in buffing aluminum is finely pulverized tripoli bound with tallow, beeswax, stearic acid, paraffin, or mixtures of these substances, into cylindrical sticks and roughly rectangular cakes. The heat of friction as these products are held against the revolving wheel softens the grease binder and the abrasive adheres to the wheel. Tripoli pastes containing a lubricant that is brushed on also may be used. To ensure close contact with the work, buffing wheels are operated at a speed of from 7000 to 8000 fpm.

The wheels for coloring generally are made of open muslin or flannel rather than the sewed buffs employed in buffing and are revolved at speeds of 7,500 to 10,000 fpm. Greater softness and flexibility in the wheels are achieved by the use of spacers. The abrasives ordinarily incorporated into the grease binder for this process are Vienna lime or soft silica, although when combined with very high wheel speeds and light pressure, grease frequently may be omitted.

Polishes and Cleaners

Silver Polishes—Silver polishes may be of five kinds—liquid, paste, powder, cake, and impregnated cloths. Federal Specification P.P.-57 lb

covers the first three of these. Soap, mineral oil, and glycerin are important ingredients of such polishes and color and perfume sometimes are added for market appeal.

A polishing medium for silver must have good tarnish-removing properties and produce a high luster; it must not scratch nor discolor the metal, nor leave any residue that will cause discoloration, not removable by washing in warm soapy water; and it must be free from acids or cyanides. Pastes and powders should not show caking tendencies and abrasive matter in liquid polishes should be resuspended readily by shaking.

Although diatomaceous earth is the most generally used abrasive in silver polish, other products employed are chalk or whiting and amorphous silica. The latter, although a rather harsh abrasive for fine silver, sometimes has been used where stronger abrasive action is necessary, particularly in creamy pastes and liquid polishes.

Cakes or bar silver polishes may contain abrasives only compressed into a suitable mold, or be composed of soaps and one abrasive or a mixture of abrasives to obtain the desired texture or color, such as a red preparation consisting of prepared chalk, jeweller's rouge and red and white tripoli.

Auto Polishes—In the compounding of auto polishes, sometimes it is desired to effect cleaning, polishing, and waxing in one operation; a liquid polish usually is employed for this purpose. This type of compound generally contains a comparatively high proportion of soft and hard waxes and often carries rather large percentages of abrasive cleaners. On the other hand, one product may be used for cleaning and another to supply a hard durable wax finish. For prewaxing compounds, pastes usually are preferred, although liquid products are widely used. They contain a high ratio of abrasive materials and facilitating products, such as solvents, polish oils, emulsifying agents, and certain waxes. Very mild abrasives such as tripoli and diatomaceous silica, either alone or together, are employed as the smoothing agent in both the "triple action" and the prewax compounds. Small amounts of bentonite almost invariably are added, not only as an active emulsifier but to prevent excessive settling, caking, or segregation of the various ingredients of the composition.

Cleaning and Polishing Cloths—Tripoli is used in the preparation of special abrasive cloths for cleaning and polishing metals particularly. Other very fine materials—rouge, whiting, kaolin, and so forth—may also be employed for this purpose. The type of surface to be cleaned determines the fineness and hardness of the abrasive or abrasive mixture chosen for treating the cloth. Thus cloths for polishing silver and aluminum require the so-called softer abrasives. Treatment of the cloth involves immersion of wool fabrics, cotton flannel, or sometimes muslin

or other materials, in a binding solution such as soap, paraffin, oils or fatty acids, or a combination of them, containing in suspension the finely divided abrasives, and removing excess liquid by pressure and drying. Color or perfuming compounds and hygroscopic agents are sometimes added. Impregnated cloths treated in this or similar manner are effective for many metals other than those mentioned above.

Glass Cleaners—Heavy, clinging, dirt films may be removed from glass surfaces by cleaning products containing mild abrasives such as precipitated chalk, calcined magnesia, crocus or rouge, tin oxide, and fine siliceous materials, including tripoli. Natural or chemical soaps and solvents are added to assist in the cleansing of greasy surfaces. These products are available as pastes, powders, cakes, or liquids.

Foundry Facing

Many foundries use tripoli as a facing or dusting material for molds. Because of its porosity and affinity for soaking up moisture, tripoli used as a foundry facing or parting is "waterproofed." Stearic acid or tallow are the principal coating agents and are used either alone or in various combinations. Other components of these mixtures may be tristearin, paraffin, oleates, and small amounts of waxes and similar materials. These substances are dissolved in solvents such as various petroleum derivatives and mixed with the tripoli under high temperatures or added directly to the melted fatty coating materials. In either case, long-continued agitation is necessary to coat any large proportion of the individual particles.

Concrete Admix

Tripoli is used extensively as an admix for cement and concrete products such as cement stucco, mortar, plaster, finishing, topping, floors, pavements, and curbs. The material must be finely ground. It is shipped in 100-lb paper-lined jute bags. The tripoli does not shrink or swell when wet. Its porosity allows quick absorption of water and, through interaction with water and cement, it coats all aggregate particles, thus having a lubricating effect. The workability and flowing properties of the mix are thereby greatly increased. The tripoli also prevents segregation during long truck hauls. Greater early and ultimate strength, decreased efflorescence, high impermeability to moisture after setting, and increased resistance to weather, sulphates, acids, oil, industrial wastes, and other corrosive substances are among other advantages claimed. It also promotes a dense structure without honeycombing and allows thorough and even curing. This material has the additional advantage of neutralizing any excess of free lime and of checking any tendency of the concrete to disintegrate.

Dry Cleaning, Laundering and Other Uses

Tripoli acts as an absorbent for fats, greases, and stains in dry cleaning. The most delicate silks and laces, it is asserted, are not injured and colors and patterns are freshened. Added to laundering baths, tripoli is said to be effective as an absorbent for greases, oils, and other foreign matter.

Metal polishes and polishes for lacquer and similar surfaces often contain tripoli as the mild abrasive. Phonograph records may contain tripoli as a filler. It may be used as a filler in paints, stains, and rubber; as a polishing medium for mirrors and glassware, for stone products such as marble, and as a mild abrasive or smoothing agent on precious stones, horn or shell products. It is also used as a finish polishing agent in the form of a thick water-mixed paste for plastics, particularly cast phenolic parts. Tripoli can be employed as a carrier in tree-dusting sprays and other insecticidal or germicidal preparations. It is used to a limited extent in water filtration, wine clarification, or other filtering, including chemical products. Its "soft," mildly abrasive properties permit its incorporation into soap and scouring powders, hand soaps or pastes.

MARKETING AND PRICES

The crude silica, when sold unprocessed, is marketed largely direct to grinders or users. The refined products, however, are sold not only direct to consumers but also to brokers or jobbers and to various trade-supply houses, and through them are distributed to local purchasers. Usually packed in paper or paper-lined jute sacks, the weight per unit of sale varies from 50 lb to more than 200 lb, exclusive of the container. Filter stones generally were made to order and sold by volume. Over a period of years, close business contact has been established between producer and consumer. Consumers often are very reluctant about changing their source of supply, as the range of specifications submitted for a new product is insufficient for predicting behavior in actual practice. Slight variation in analysis or physical properties of the raw material also may effect decidedly unfavorable and troublesome changes in the consumer's end product.

Prices of tripoli, rottenstone, and amorphous silica over a period of years have changed but little and have reflected a comparatively stable price situation. Quotations on "Illinois silica" and on tripoli are carried regularly in the *Engineering and Mining Journal's* department on Metal and Mineral Markets and quotations on "Illinois amorphous silica," rottenstone, and tripoli have appeared in the *Oil, Paint and Drug*

Reporter. All of these series as presented in the periodicals mentioned have remained at the same level over a period of several years. Toward the end of 1947 (Dec. 11), the quoted prices in E. and M. J. Metal and Mineral Markets were: for Illinois silica, 92 to 99.5 pct grades, water-ground and floated, in bags, f.o.b. shipping point, 325-mesh, \$21 to \$40 per short ton; and dry-ground, air-floated, 375-mesh, \$18 to \$30. In the same issue of E. and M. J. Metal and Mineral Markets, Missouri tripoli on an f.o.b. basis, in paper-lined burlap bags, minimum carload, 30 tons, was quoted as follows: rose and cream-colored, once-ground through 40-mesh, \$14.50; rose and cream-colored, double-ground through 110-mesh, \$16; and air-floated through 200-mesh, \$26.

Quotations on the types of silica noted above as given in *Oil, Paint and Drug Reporter* of Dec. 26, 1947, were as follows: amorphous silica, in bags, carlots, f.o.b. Illinois works, dry-ground 325-mesh, \$17 per short ton; 400-mesh, \$18; wet-ground minus 325-mesh, \$18 per ton; 400-mesh, \$18 per ton; 96 to 98 pct silica, 325-mesh, \$20 per ton and 99 pct silica, 325-mesh, \$20 per ton. Tripoli quotations at works, carlots, in bags according to the same source were: Air-float, \$21.50 per short ton; double-ground, \$17.50 per ton and once-ground, \$16 per ton. Carlots of rottenstone, packed in bags, were quoted at \$25.50 per short ton, f.o.b. mines, and less than carlots, at \$37.50 per ton.

FOREIGN TRADE

Imports—Imports of tripoli and rottenstone have been combined with diatomaceous earth in official foreign trade statistics. Although the figures for rottenstone and tripoli are somewhat obscured by this treatment, receipts of these minerals over a period of years are listed in Table 8. It is not possible to verify it definitely, but most of the material imported from Algeria-Tunisia and Canada probably should be considered as diatomaceous earth or kieselguhr. Judging by the high average values indicated, many of these import shipments apparently have been subjected to intensive preparation.

Exports—No separate data are available to indicate actual quantities of tripoli, amorphous silica, or rottenstone exported by the United States. It is understood, however, that only the Missouri-Oklahoma tripoli has been exported in appreciable amounts. Tripoli pulverized and graded into specific sizes suitable for buffing and polishing has been shipped to many countries of the world. The largest tonnage is said to be consumed in the United Kingdom and smaller amounts are shipped to Germany, the Netherlands, France, and other European countries. Shipments also have been made to South America, Canada, India, and the Far East. In normal times, it is understood that total exports may aggregate several thousand tons a year.

TABLE 8—Imports of Tripoli, Rottenstone, and Diatomaceous Earth, United States, 1934–1947

Country	1934		1935		1936		1937	
	Long Tons	Value	Long Tons	Value	Long Tons	Value	Long Tons	Value
Belgium.....					11	\$ 229	11	\$ 356
Spain.....	132	\$ 3,036	98	\$ 2,036	25	568		
United Kingdom....	6	380	11	685	7	327	1	160
USSR (Russia).....			761	5,247				
Algeria-Tunisia.....	45	709	40	613	704	2,318	608	6,714
Canada.....	1,184	33,578	509	16,226	216	7,703	155	4,884
Brazil.....							1	18
Other countries.....	50	150	1	118	3	614	2	75
	1,417	37,853	1,420	24,925	966	11,759	778	12,207

Country	1938		1939		1940		1941	
	Long Tons	Value	Long Tons	Value	Long Tons	Value	Long Tons	Value
Belgium.....	19	\$ 530	2	\$ 99				
United Kingdom....	1	183	1	174	1	\$ 49	2	\$ 181
Algeria-Tunisia.....	195	1,803	138	1,191	20	159		
Canada.....	121	5,775	21	851	5	358	6	355
Mexico.....	105	1,325	4	54	172	3,001	353	7,547
Brazil.....			4	163	5	200	22	903
Other countries.....	4	210	25	237			2	130
	445	9,826	195	2,769	203	3,767	385	9,116

Country	1942		1943		1944	
	Long Tons	Value	Long Tons	Value	Long Tons	Value
United Kingdom.....	5	\$ 283				
Canada.....	6	383	5	\$268	3	\$60
Mexico.....	195	4,160				
Other countries.....						
	206	4,826	5	268	3	60

Country	1945		1946		1947	
	Long Tons	Value	Long Tons	Value	Long Tons	Value
Canada.....			6	\$ 217		
Mexico.....	33	\$1,170	77	2,878	74	\$2,951
	33	1,170	83	3,095	74	2,951

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CHAPTER 51

VERMICULITE

By JOHN B. MYERS*

VERMICULITE is a name used to describe micaceous material that exfoliates when heated. It is hydrated magnesium-aluminum-iron silicate. The chemical composition, color, physical appearance, and degree of exfoliation vary.

COMPOSITION, PROPERTIES, AND ORIGIN

Vermiculite has the characteristic micaceous structure of basal cleavage and readily splits into thin laminae, which are soft, pliable, and inelastic. The monoclinic crystal faces are often marked by triangular lines at 60° and 120°. Hardness is 1.5; specific gravity, 2.2–2.7; luster pearly to greasy; colors, amber, bronze, reddish brown, dark green, and black. Feel is soapy, particularly when wet. When heated it exfoliates by expanding at right angles to the cleavage into long wormlike pieces (the name vermiculite is from the Latin *vermiculari*, to breed worms). This important characteristic of expansion is believed to be a mechanical separation of the layers when the contained water is converted into steam. Warping of the unit layers may also contribute to the expansion. The increase in bulk volume of commercially prepared material is 8 to 12 times but individual flakes may increase in size more than this.

Pure vermiculite is a distinct mineral and has the structural formula $(\text{OH})_2 (\text{Mg}, \text{Fe})_3 (\text{Si}, \text{Al}, \text{Fe})_4 \text{O}_{10} \cdot 4\text{H}_2\text{O}$. It rarely occurs in this pure form, but generally as a mixed mineral of varying structure. One explanation is that the mixed material is composed of unit layers of interstratified pure vermiculite and biotite. The essential difference between the two is that unit cell structure of vermiculite contains a layer of water molecules whereas the biotite cell contains potassium instead of the water. The water content of the mixed vermiculite is less than that of pure vermiculite but more than that of biotite. Pure biotite does not expand when heated. If the proportion of biotite layers in a vermiculite is too high it will adversely affect the degree of exfoliation. Within a given deposit, the great mass of material may approach a definite composition with local areas of greater biotite content. It is not uncommon to find also small pockets of pure biotite but these are generally segre-

* Vice-President Zonolite Company, Chicago, Ill.

gated. The occurrence and close relationship of these related micas in the same deposit causes considerable variation between materials that are all identified as vermiculite. Commercial vermiculites are those that expand readily to a light-weight material.

Vermiculite and the associated micas were formed by the hydrothermal alteration of an ultrabasic igneous stock, generally pyroxenite. It was once thought that the vermiculite was formed by the hydration of biotite but a detailed study of the large deposit near Libby, Montana, has shown that the vermiculite was formed by the alteration of the pyroxenite. Whether the alteration produced vermiculite or biotite, also the proportions and segregations of each, was determined largely by the chemical composition of the hydrothermal solution, particularly the presence of potassium. The entire process was very complex and in several stages. Most deposits are intruded by extensive dikes, generally of syenite. It has been reported that the vermiculites of North Carolina were formed by hydration and alteration of chlorite. It is likely that vermiculite has been formed by several geologic processes.

DISTRIBUTION OF DEPOSITS

Vermiculite deposits are widespread and have been reported from most parts of the world. It is still a relatively new material commercially and when it becomes better known to prospectors, undoubtedly many more deposits will be found. Most of the known deposits are not commercial by present standards, so the number of active mines is still relatively small. There is currently much exploration and development activity and new commercial deposits are being found.

United States—There are deposits of vermiculite in Arizona, California, Colorado, Georgia, Montana, Nevada, New Mexico, North Carolina, Pennsylvania, South Carolina, Texas, and Wyoming. The principal producing states are Colorado, Montana, North Carolina, South Carolina, and Wyoming. At the present time, the largest production is from Montana and the second largest from South Carolina.

World—Deposits have been reported in Australia, Brazil, Chile, Cuba, Ethiopia, Japan, Kenya, Mexico, Russia, Tanganyika, and Union of South Africa.

POLITICAL AND COMMERCIAL CONTROL

The development of vermiculite as a commercial material has been almost entirely the work of a few companies in the United States. The principal market has been developed in this country but a considerable world market has been developed also. Regular shipments of vermiculite (unexpanded) are made to five manufacturing plants in Canada. These in turn expand the material and market it throughout Canada. There are also exports to Mexico, India, Venezuela, Puerto Rico, Brazil, and before the war, to Australia, Burma, and Singapore.

South Africa is now developing its local market and has exported to India, Canada, and the United States. Plans are being made to introduce the South African material into the large American market in competition with the American production.

PRODUCTION AND CONSUMPTION

In the initial development stage of the industry, there was no established market for vermiculite, and the usefulness of the material was only vaguely understood by the original producers. The unusual characteristics of the exfoliated material suggested many industrial uses. The years of small production were the years of research, development, and market pioneering that established its utility and built the present

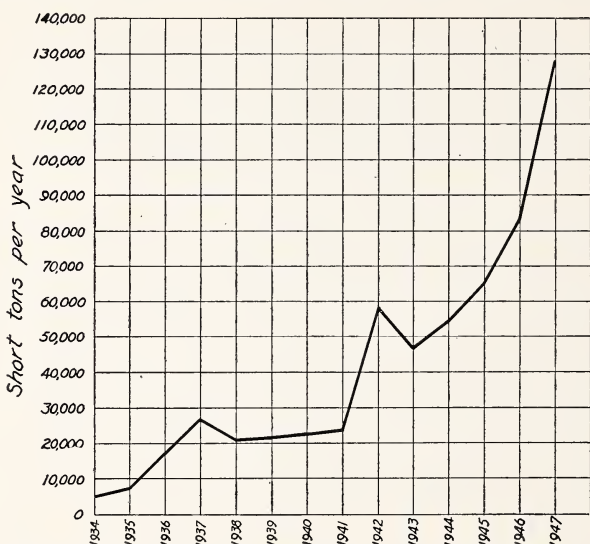


FIG 1—PRODUCTION OF VERMICULITE, UNITED STATES.

market. As the market grew, corresponding production facilities were built, which were in themselves formidable development problems. Except for brief periods, production has kept pace with demand.

United States—Although vermiculite was first discovered and its exfoliating properties described in 1824, there was no commercial production until 1915, when a small amount was produced near Salida, Colorado. During the next 10 years, small amounts were produced from other Colorado deposits. Development of the deposit near Libby, Montana, began in 1919 and the first shipments recorded were in 1925, when 2 tons was shipped. Production in the United States remained very small until 1934. The production since then is shown in Fig 1.

World—Foreign production has remained small until recently. The principal production outside the United States is in the Union of South Africa, which started in an experimental way about 1938. A

few shipments were made to India during the war when the American supply was cut off. There are now at least three producing mines in South Africa, as well as other properties that intend to produce. Most of the production is from a deposit in the northern Transvaal. Additional production facilities were built in 1946 and there is currently much activity, and the plans are to export into the world market. There has been some production in Australia, Brazil, and Chile for local use. Production has been reported in Russia and there was at least one shipment to the United States but there is no recent information.

PROSPECTING AND EXPLORATION

Prospecting—Vermiculite is not a conspicuous material and there are no prominent outcrops. The first evidence in the field is likely to be scattered flakes in the soil or in a stream bed. A gulley through the deposit will generally expose the ore body. Vermiculite is often found during other mining activities. Roadcuts have exposed some deposits.

Vermiculite deposits are in the form of an igneous intrusive or plug of ultrabasic rock that has been altered to vermiculite. Therefore an area containing ultrabasic outcrops is more likely to have vermiculite, particularly if these outcrops are cut up by pegmatites. These clues have been used with some success in the southeastern states. Vermiculite is often overlooked because micaceous flakes are widespread and common in many areas. Closer examination may show that some of these flakes are vermiculite.

Exploration—After the first field evidence of vermiculite, the next step is to locate and uncover the ore body. Since this is largely a matter of exposing the underlying rock in place, a bulldozer can do this very effectively and is generally used. The nature of a deposit can be determined by studying the exposed surface.

The first characteristic required in a commercial deposit is the quality of the mineral. It must readily expand to a high degree when heated, it must not contain a large amount of admixed biotite, and it must be predominately in the flake sizes required by the market. Large flakes may be crushed but very small flakes are not in demand. The second requirement is that the percentage of vermiculite in the rock mass must be fairly high. The present practice is to mine only ore that contains 40 pct or more of vermiculite. However, the industry is now doing extensive research to develop commercial methods of economically utilizing material of lower vermiculite content. When this program is successful it will have the effect of vastly increasing the ore reserves of this country.

The third characteristic of a good deposit is that the ore body be large and massive. The many occurrences of vermiculite in the form

of small veins and scattered pockets have not been successful. The massive ore body lends itself to a power-shovel operation, which is required to get low cost. Transportation is also an important consideration and an otherwise good deposit will not be commercial if it is too remote and the cost of hauling to a railroad too expensive.

If the exposed ore body has the characteristics outlined above, it is further developed by stripping or terracing with a bulldozer to determine area and is explored at depth by drilling and digging adits and shafts.

MINING METHODS

Almost all the vermiculite produced in the United States is mined by open-pit methods with a power shovel. One small deposit has been mined with a dragline and another with a bulldozer and loading conveyor.

The deposit near Libby, Montana, is a large, rounded hill, almost all of which contains vermiculite. The entire top of this hill is being mined off in benches about 16 ft high. Two power shovels, of 1 $\frac{1}{4}$ -yd and 2-yd capacity, are used. All waste material is moved currently so that the entire level is advanced. Formerly the ore was loaded into trucks having pneumatic tires and was hauled to the mill bins. Now the shovels load into 12-ton trucks equipped with crawler tracks in the rear. The vermiculite ore is soft and spongy and this type of equipment is more successful than standard trucks during wet weather. The half-track trucks haul to a primary plant at the edge of the deposit, which is also the location of the waste dump. Here the ore is screened and the plus 3-in. material goes over a picking belt, where the large pieces of vermiculite are picked off and passed through a hammer-mill crusher. There is very little of this oversize. The undersize and the crushed oversize are then conveyed 1300 ft to the mill bins, on a 24-in. conveyor belt.

The deposits in South Carolina are smaller and the ore is generally high grade. Smaller shovels are used, which load directly into standard 10-wheel trucks that haul directly to the processing plant.

PREPARATION FOR MARKET

Vermiculite must be exfoliated (expanded by heating) before it is used. There are practically no uses for the unexpanded mineral. The expanded material weighs from 4 $\frac{1}{2}$ to 10 lb per cubic foot, depending on the size and kind and is therefore too bulky to ship long distances, but the unexpanded material is fairly heavy and can readily be handled in bulk by ordinary means. The significant property of exfoliation makes it possible to ship from the mine to the market in a concentrated form and produce the light-weight product near the market. All of the

preparation from the mine to the ultimate market is influenced by this basic idea.

Vermiculite ore is prepared at the mine site, so that when it is shipped to the expanding plant and exfoliated it will be a finished product ready for the various market requirements. The ore must be dried to a moisture content best suited to the expanding furnace and concentrated to a specified vermiculite content; also, it must be screened into the various particle sizes that are required for the final expanded products. The oversize particles are crushed to size and the very small particles are removed. Some deposits are very pure and the ore does not need concentration; for instance, the deposits in South Carolina.

Without concentration, the milling is as follows: The mine-run material is dumped through a 3-in. grizzly for removal of large chunks, then goes to ore storage. From storage it is taken by feeder and conveyor to a rotary tube drier, which is parallel flow and direct-fired with oil heat, elevated to vibrating screens, where the oversize is removed, and returned to a hammer-mill crusher in a closed circuit with the bucket elevator and screen. The screens further divide the ore into the market sizes and remove the very fine dust. The finished sizes are stored in bins ready for shipment to the expanding plants.

When the ore must be concentrated, this same pattern is followed and the concentrating is done after the material is divided into the various sizes. Many concentrating devices have been used and there is still much experimentation in the industry. Different methods are required for high-grade and low-grade ores and for the physical variations in the ores from different deposits. The following concentrating methods have been used or reported: air classifiers, pneumatic tables, screening over alternate square-mesh and slotted screens, winnowing, roll crushing (which shatters the cubical rock in preference to the flaky vermiculite), electrostatic separation, agglomerate tabling, froth flotation of fines, jigging, and tabling. None of the known mills uses any of the wet processes.

The present commercial sizes are: minus $\frac{1}{2}$ -in. plus 3-mesh, minus 3 plus 14, minus 8 plus 20, minus 8 plus 65, minus 10 plus 65, minus 20 plus 100 (Tyler standard screen sizes). The prepared vermiculite concentrate is shipped in bulk in boxcars. When it reaches the expanding plants, it is mechanically unloaded and conveyed to bins. The material is fed at a constant rate into a bucket elevator, which drops it into the top of a vertical, oil-fired furnace that exfoliates the vermiculite very rapidly at a temperature of about 2000°F. The exfoliated material is then conveyed to an air separator that removes any remaining rock, from which it goes into a cooling device that reduces the temperature, for easy handling. The finished material is packaged in paper bags of 4-cu ft capacity.

TESTS AND SPECIFICATIONS

Vermiculite concentrates are tested for screen analysis, ignition loss when expanded, impurities, and volume yield. The different sizes usually are designated by the overall Tyler standard screen sizes, such as minus 3 plus 14, minus 8 plus 20. Specifications provide for a certain allowable percentage of oversize and undersize. Samples are tested on a Ro-Tap tester for 7 min. The ignition loss is the total free moisture and combined water loss when the material is completely expanded. Testing is by expanding a weighed sample in an electric muffler furnace at 1800°F for 5 min., or until expansion is complete. Specifications generally call for material predried to an ignition loss not exceeding 10 pct.

Impurities are tested for by expanding a weighed sample as in the moisture test, cooling, then floating off the expanded vermiculite with water and washing the residual waste. The impurities are dried and weighed and expressed in terms of the weight of the unexpanded sample. Specifications generally limit the impurities to 10 pct for the larger sizes and 15 pct for the smaller.

Since there are differences in the inherent expandability of different vermiculites, the volume to which a given size will expand is important to the purchaser of vermiculite concentrates. This is expressed as cubic feet of expanded material per ton of concentrate. The only reliable test method is to process a sizable sample in a commercial furnace. Specifications often call for minimum yields for each size. The larger screen sizes have greater yields than the smaller sizes.

The expanded material often is specified in terms of weight per cubic foot and is tested by weighing a cubic foot measure. Expanded vermiculite concrete aggregate is usually made to conform to American Society for Testing Materials Designation C33-42, standard specification for fine concrete aggregates. Expanded vermiculite plaster aggregate is usually made to conform to ASTM Designation C35-39, standard specification for sand in plaster. Material used in certain fireproofing applications is made to conform to Underwriters Laboratory specifications for the particular rating that is desired. The industry has organized a Vermiculite Institute, which has issued specifications for many applications of expanded vermiculite.

MARKETING AND USES

Generally the mining companies that produce and market vermiculite concentrates also have expanding plants and produce and market expanded vermiculite. Many companies buy vermiculite concentrates and manufacture expanded vermiculite products but only a few companies mine the ore. Some of the mining companies license the manu-

facturing companies under various patents and processes to manufacture and sell in restricted territories. The manufacturer of expanded vermiculite products sells through jobbers, dealers, and sometimes to contractors who make the final installations. Materials like home insulation, concrete aggregate, and plaster aggregate are sold almost entirely through lumber and building-material dealers. These products are now available throughout the United States and Canada and are sold under several brand names.

The characteristics of expanded vermiculite that make it a useful material are: its thermal insulating qualities, its light weight, its fireproofness, and its granular form. The principal uses are applications of one or more of these characteristics. The larger granules are used as a loose fill insulation for homes, industrial structures, farm buildings, cold storage, refrigeration, high-temperature refractory surfaces, and in all types of high-temperature and low-temperature industrial equipment.

The medium-sized granules are graded to make aggregates for insulating concrete and plaster. Plaster aggregate is used in wall plaster in the same way that sand is used by mixing with ordinary gypsum and water. Plaster made with vermiculite aggregate has the following properties: It is extremely fireproof; it will internally absorb impact and strain, which makes it crack resistant; it has insulating and sound-absorbing value; its light weight is a structural advantage and also makes it easy for workmen to handle and apply. There is also a product manufactured especially for acoustical work, which is troweled over walls and ceilings for sound absorption.

Concrete aggregate is used with portland cement and water to form a light-weight insulating concrete. In order to be successful, there must also be a stabilizing agent to prevent segregation, breakdown, or loss of air from the particles during the mixing and placing of the concrete. Several materials are used as stabilizers and are either added to the aggregate during manufacture or added to the concrete while it is being mixed on the job. The cement is used in different proportions according to the strength required. Vermiculite concrete is used for roof insulation, floor insulation and insulating structural roof decks, and is precast into blocks and tiles for a great variety of fireproofing, insulating, and dead-weight-saving applications.

Expanded vermiculite is used in horticultural work, where its properties of holding air and water make it useful for root development and for starting seeds and cuttings. It is also used as an additive for conditioning soil. Expanded vermiculite is manufactured into insulating refractory bricks and blocks, insulating plastics, pipe lagging, roof-insulation blocks, and other products. There are many other diverse uses, such as its use for poultry litter, as a lubricant, or as a filler.

PRICE HISTORY

Unexpanded vermiculite concentrates have been very steady in price during the past 10 years. Postwar price increases were nominal. Present prices of cleaned, dried, and sized Montana material, f.o.b. cars, are: for the larger sizes, \$13.50 a ton; for the smaller aggregate sizes, \$12 a ton. Present price of aggregate material in South Carolina is \$12 a ton, f.o.b. cars.

After this material is shipped to the expanding plants, exfoliated, and packaged in paper bags, the prices vary considerably because of the many uses for which the different sizes are prepared and the location of the expanding plant with reference to the mines, which determines the freight charges. (Example: The present freight rate from Montana to Chicago is \$10 a ton and from South Carolina to Chicago, \$8.75 a ton.) A package containing 4 cu ft of average-priced material would be sold by a Midwest manufacturer to a jobber for about \$0.90, which would make the dealer's cost about \$1.00. The price to the consumer would be determined by the handling costs, freight, and the dealer's mark-up. The different products sell for different prices.

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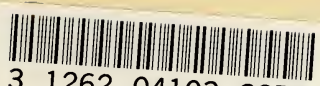
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